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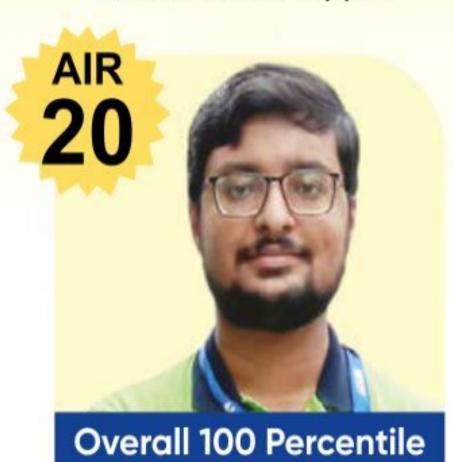


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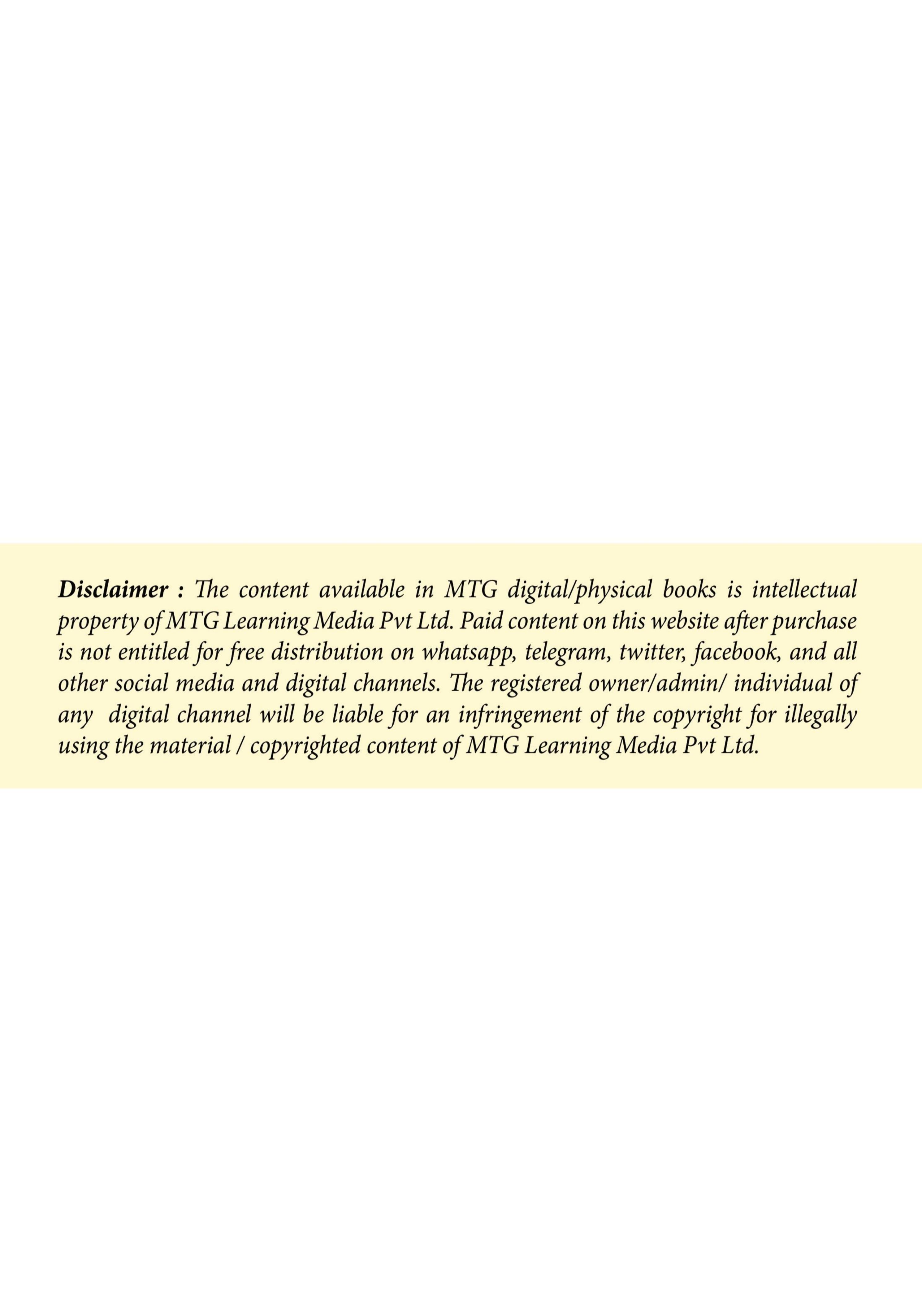


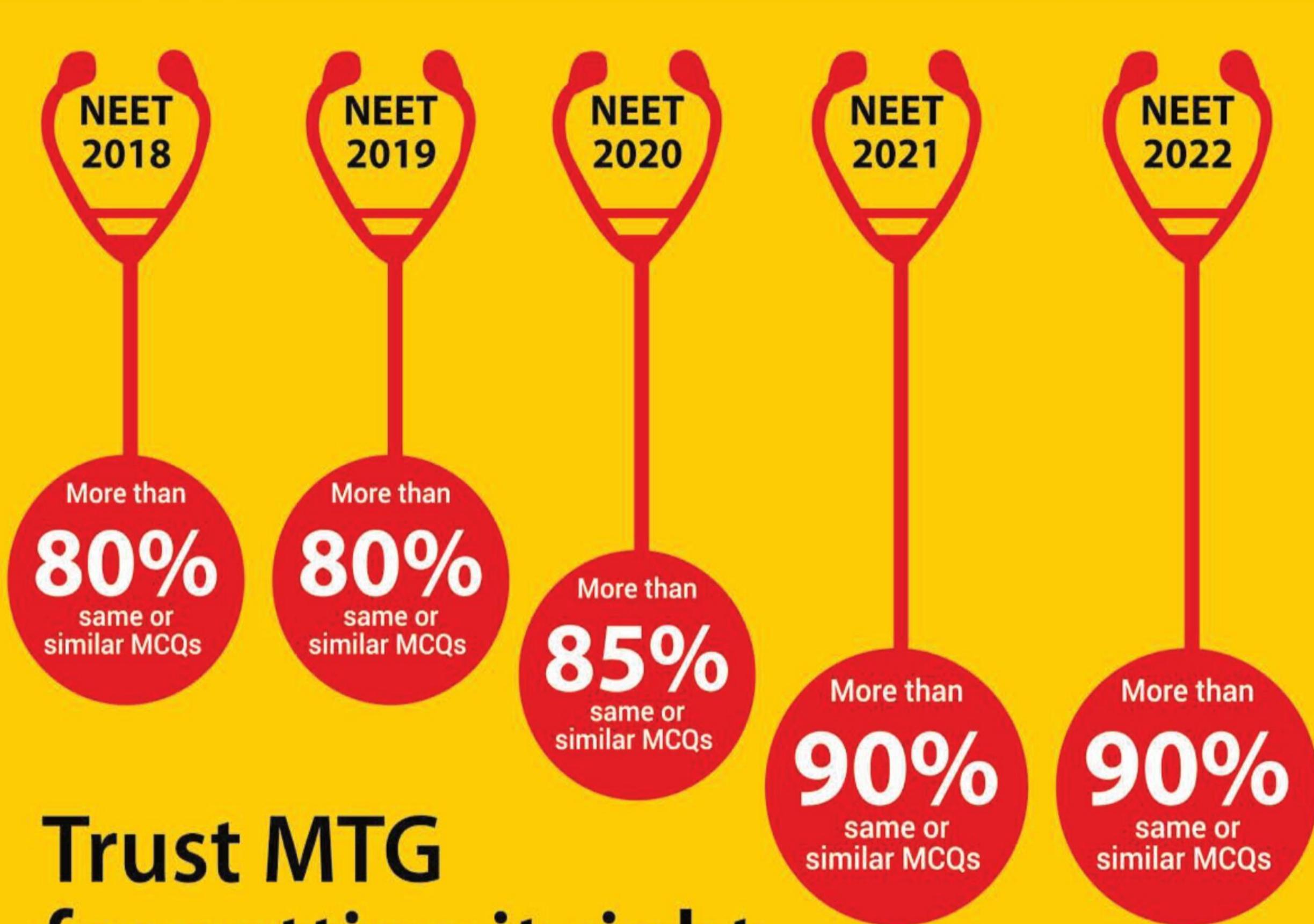


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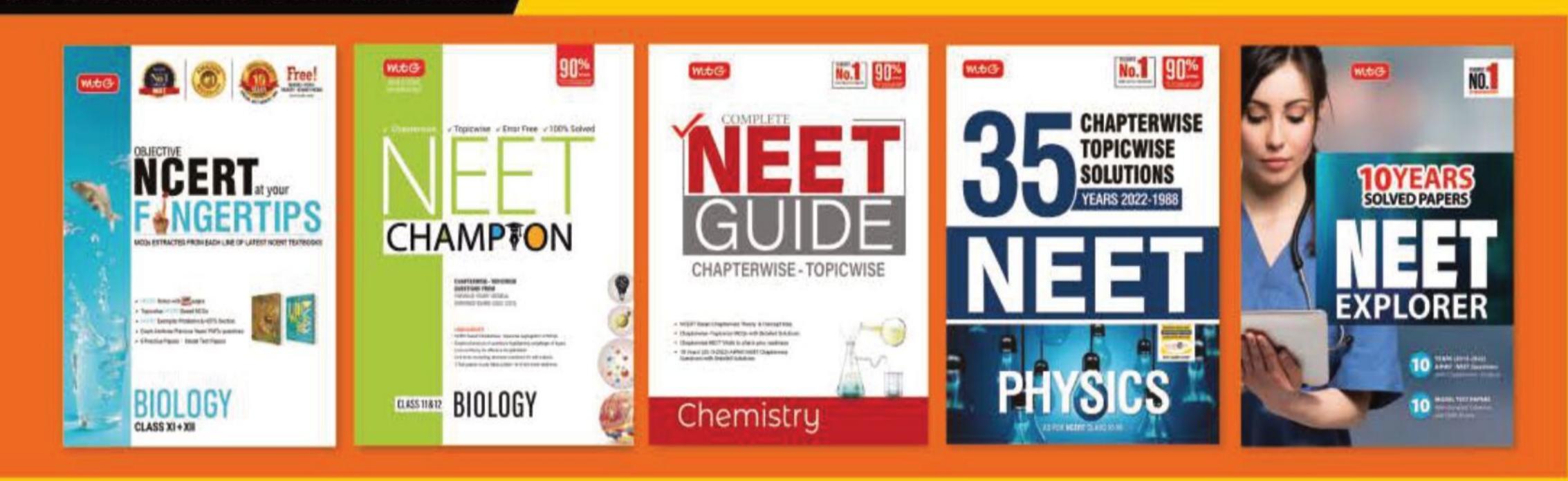


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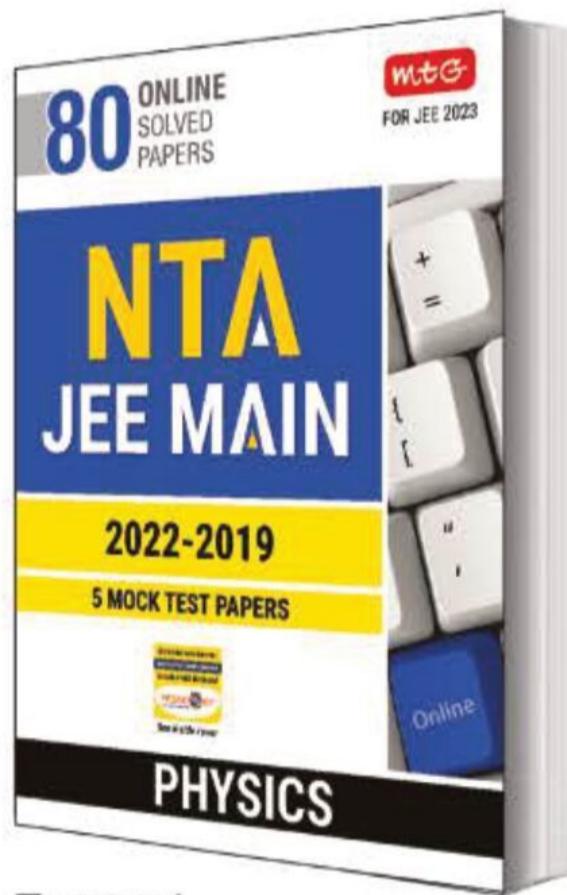


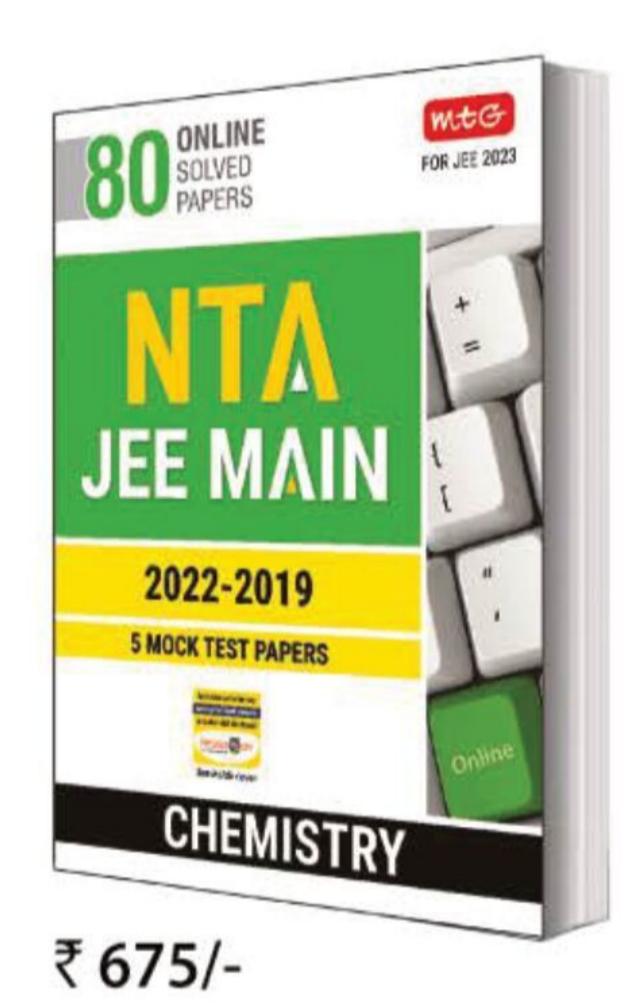


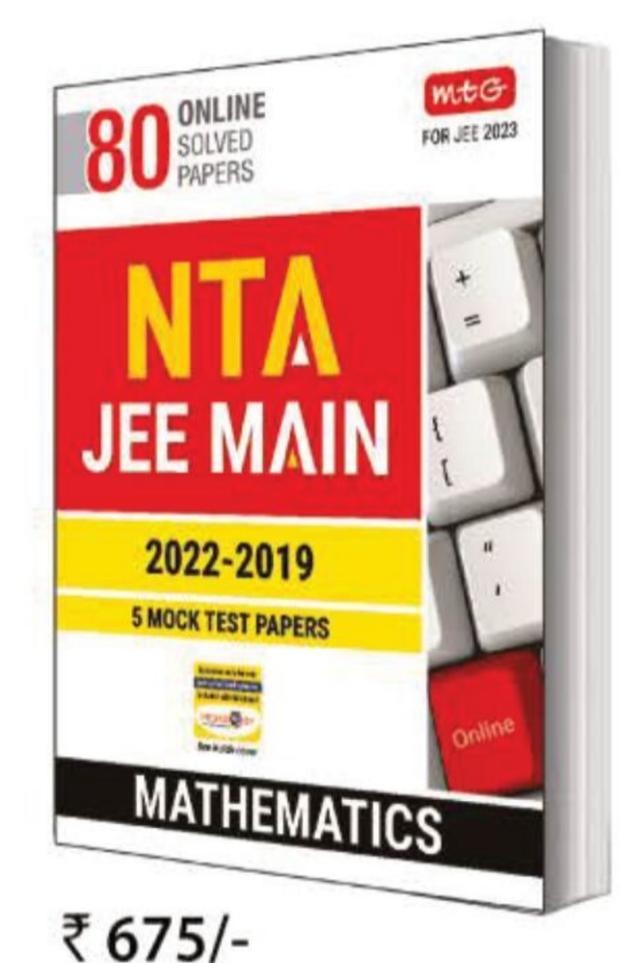
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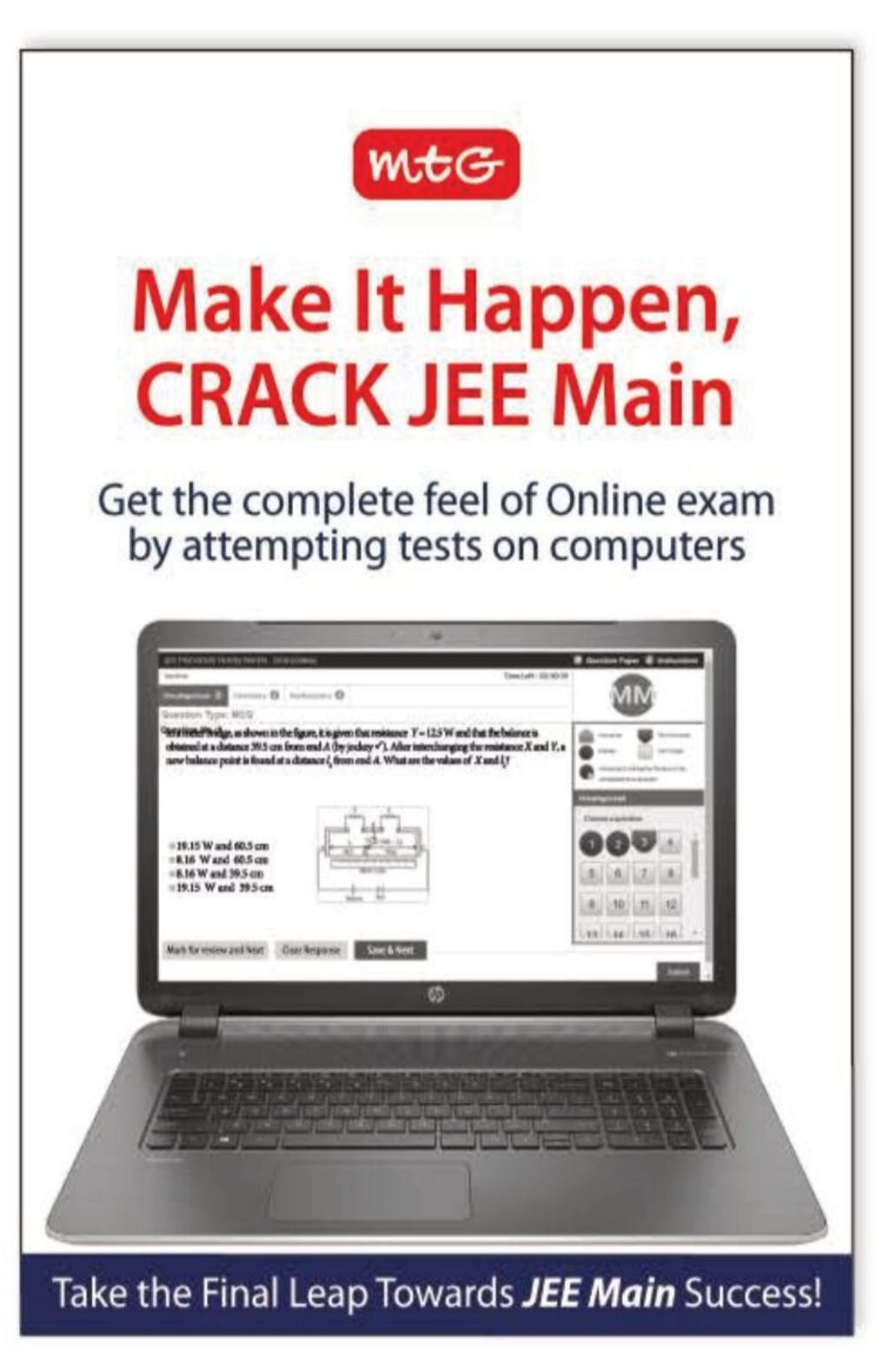
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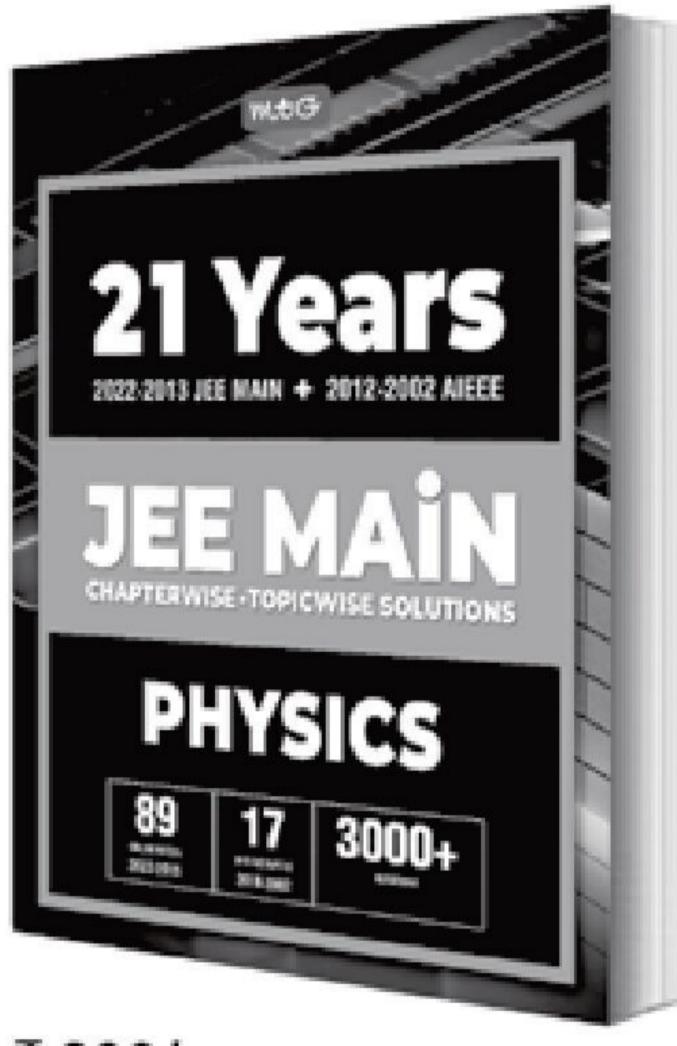
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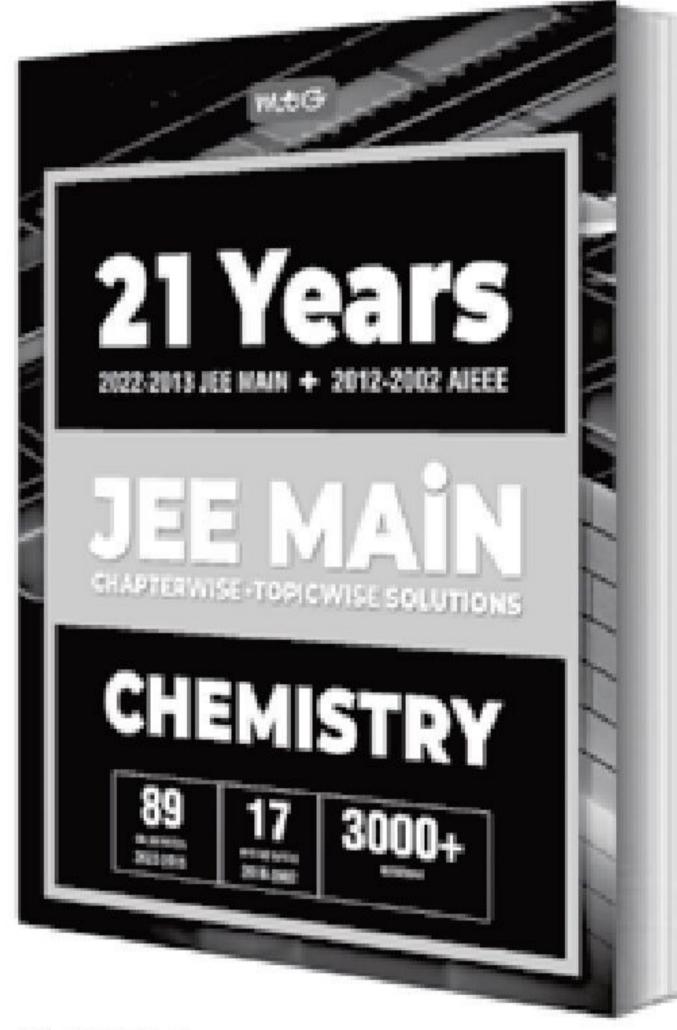
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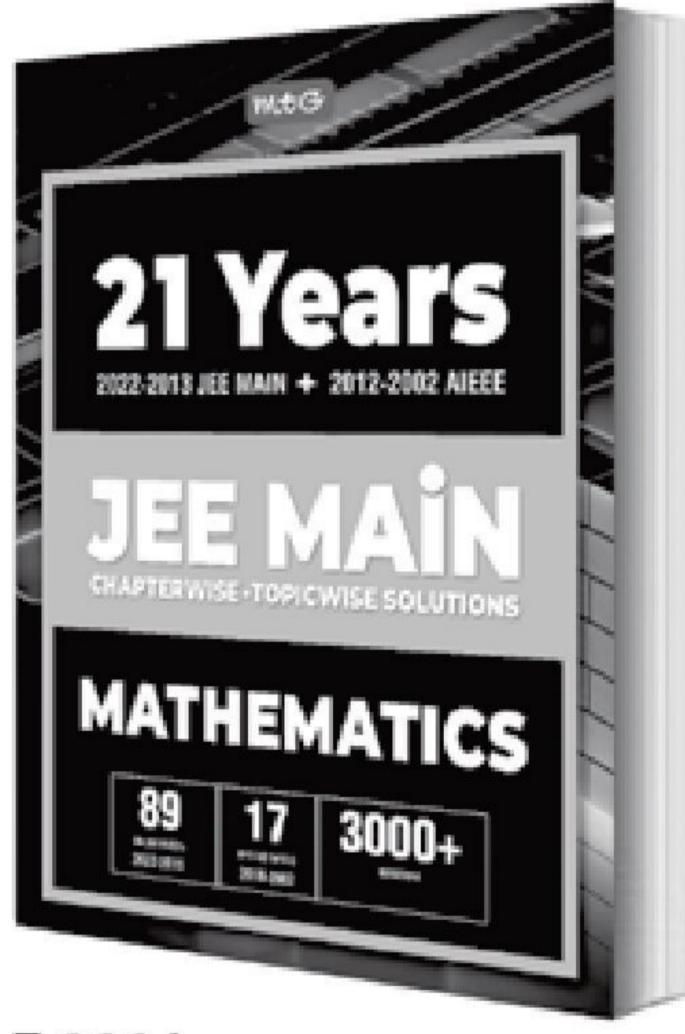


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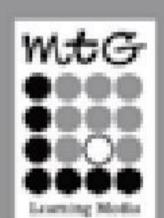
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Held on 25th July, Morning Shift

SECTION-A (MULTIPLE CHOICE QUESTIONS)

1. SO₂Cl₂ on reaction with excess of water results into acidic mixture

$$SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

16 moles of NaOH is required for the complete neutralisation of the resultant acidic mixture. The number of moles of SO₂Cl₂ used is

- (a) 16 (b) 8 (c) 4

- (d) 2
- Which of the following sets of quantum numbers is not allowed?

(a)
$$n=3, l=2, m_l=0, s=+\frac{1}{2}$$

(b)
$$n=3, l=2, m_l=-2, s=+\frac{1}{2}$$

(c)
$$n=3, l=3, m_l=-3, s=-\frac{1}{2}$$

(d)
$$n=3, l=0, m_l=0, s=-\frac{1}{2}$$

- 3. The depression in freezing point observed for a formic acid solution of concentration 0.5 mL L⁻¹ is 0.0405°C. Density of formic acid is 1.05 g mL⁻¹. The Van't Hoff factor of the formic acid solution is nearly (Given for water $k_f = 1.86 \text{ K kg mol}^{-1}$)
- (a) 0.8 (b) 1.1 (c) 1.9
- (d) 2.4
- 20 mL of 0.1 M NH₄OH is mixed with 40 mL of 0.05 M HCl. The pH of the mixture is nearest to (Given : $K_b(NH_4OH) = 1 \times 10^{-5}$, log 2 = 0.30, $\log 3 = 0.48$, $\log 5 = 0.69$, $\log 7 = 0.84$, $\log 11 = 1.04$) (a) 3.2 (b) 4.2 (c) 5.2 (d) 6.2
- Match List-I with List-II.

	List -I	List-II	
(A)	$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$	(I)	Cu
(B)	$CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)}$	(II)	Cu/ZnO
	$+ H_2O_{(g)}$		- Cr ₂ O ₃

(C)	$CO_{(g)} + H_{2(g)} \rightarrow HCHO_{(g)}$	(III)	Fe_xO_y
			$+ K_2O + Al_2O_3$
			Al_2O_3
(D)	$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(g)}$	(IV)	Ni

Choose the correct answer from the options given below:

(a)
$$A - (II), B - (IV), C - (I), (D) - (III)$$

(b)
$$A - (II), B - (I), C - (IV), (D) - (III)$$

(c)
$$A - (III), B - (IV), C - (I), (D) - (II)$$

(d)
$$A - (III), B - (I), C - (IV), (D) - (II)$$

- The IUPAC nomenclature of an element with electronic configuration [Rn] $5f^{14}6d^17s^2$ is
- Unnilbium (b) Unnilunium
 - (c) Unnilquadium (d) Unniltrium.
- 7. The compound(s) that is(are) removed as slag during the extraction of copper is
 - (A) CaO (B) FeO (C) Al₂O₃ (D) ZnO

(E) NiO

Choose the correct answer from the options given below:

- (a) (C), (D) only
- (b) (A), (B), (E) only
- (c) (A), (B) only
- (d) (B) only
- 8. The reaction of H_2O_2 with potassium permanganate in acidic medium leads to the formation of mainly
 - (a) Mn^{2+} (b) Mn^{4+} (c) Mn^{3+} (d) Mn^{6+}

- 9. Choose the correct order of density of the alkali metals.
 - (a) Li < K < Na < Rb < Cs
 - (b) Li < Na < K < Rb < Cs
 - (c) Cs < Rb < K < Na < Li
 - (d) Li < Na < K < Cs < Rb

10. The geometry around boron in the product *B* formed from the following reaction is

$$BF_3 + NaH \xrightarrow{450 \text{ K}} A + NaF$$

- $A + NMe_3 \longrightarrow B$
- (a) trigonal planar (b) tetrahedral
- (c) pyramidal
- (d) square planar.
- 11. The interhalogen compound formed from the reaction of bromine with excess of fluorine is a
 - (a) hypohalite
- (b) halate
- (c) perhalate
- (d) halite.
- 12. The photochemical smog does not generally contain
 - (a) NO
- (b) NO₂
- (c) SO_2
- (d) HCHO
- **13.** A compound *A* on reaction with *X* and *Y* produces the same major product but different by-product *a* and *b*. Oxidation of *a*, gives a substance produced by ants.

CH₃ CH₃ CH₃
$$\downarrow$$

$$H_2C = C - CH_2 - C - CH_3$$

$$CH_3 CH_3 CH_3 CH_3$$

$$CH_3 CH_3 CH_3$$

$$CH_3 CH_3 CH_3$$

$$CH_3 CH_3 CH_3$$

$$CH_3 CH_3$$

X and Y respectively are

- (a) KMnO₄/H⁺ and dil. KMnO₄, 273K
- (b) KMnO₄ (dilute), 273 K and KMnO₄/H⁺
- (c) $KMnO_4/H^+$ and O_3 , H_2O/Zn
- (d) O_3 , H_2O/Zn and $KMnO_4/H^+$
- 14. Most stable product of the following reaction is

$$(i) H_3C \longrightarrow SO_2Cl, Pyridine$$

$$(ii) NaCN, DMF$$

$$(a) \qquad (b) \qquad CN$$

$$(c) \qquad (d) \qquad (d)$$

15. Which one of the following reactions does not represent correct combination of substrate and product under the given conditions?

- (a) $Cl \xrightarrow{H_2} Pd-BaSO_4$ H(b) $CN \xrightarrow{(i) DIBAL-H} O$ H(c) $CO_2C_2H_5 \xrightarrow{(i) AlH(iso Bu)_2} O$ H(d) $OH \xrightarrow{(i) Na_2Cr_2O_7} O$ H
- 16. An organic compound A on reaction with NH₃ followed by heating gives compound B, which on further strong heating gives compound $C(C_8H_5NO_2)$. Compound C on sequential reaction with ethanolic KOH, alkyl chloride and hydrolysis with alkali gives a primary amine. The compound A is

17. Melamine polymer is formed by the condensation of

 NH_2

- 18. During the denaturation of proteins, which of these structures will remain intact?
 - (a) Primary
- (b) Secondary
- (c) Tertiary
- (d) Quaternary
- 19. Drugs used to bind to receptors, inhibiting its natural function and blocking a message are called
 - (a) agonists
- (b) antagonists
- allosterists
- (d) antihistaminists.
- 20. Given below are two statements:

Statement I: On heating with KHSO₄, glycerol is dehydrated and acrolein is formed.

Statement II: Acrolein has fruity odour and can be used to test glycerol's presence.

Choose the correct option.

- Both statement I and statement II are correct.
- Both statement I and statement II are incorrect.
- Statement I is correct but statement II is incorrect.
- (d) Statement I is incorrect but statement II is correct.

SECTION-B (NUMERICAL TYPE QUESTIONS)

Attempt any 5 questions out of 10.

- 21. Among the following species $N_2, N_2^+, N_2^-, N_2^{2-}, O_2, O_2^+, O_2^-, O_2^{2-}$ the number of species showing diamagnetism
- 22. The enthalpy of combustion of propane, graphite and dihydrogen at 298 K are -2220.0 kJ mol⁻¹, -393.5 kJ mol⁻¹ and -285.8 kJ mol⁻¹ respectively. The magnitude of enthalpy of formation of propane (C₃H₈) is _____ kJ mol⁻¹. (Nearest integer)
- 23. The pressure of a moist gas at 27°C is 4 atm. The volume of the container is doubled at the same temperature. The new pressure of the moist gas is 10^{-1} atm. (Nearest integer) (Given: The vapour pressure of water at 27°C is 0.4 atm.)
- 24. The cell potential for $Zn|Zn^{2+}_{(aq)}||Sn^{x+}|Sn$ is 0.801 V at 298 K. The reaction quotient for the above reaction is 10^{-2} . The number of electrons involved in the given electrochemical cell reaction is _____. (Given: $E_{Zn^{2+}/Zn}^{\circ} = -0.763 \text{ V}, E_{Sn^{x+}/Sn}^{\circ} = +0.008 \text{ V} \text{ and}$ 2.303RT/F = 0.06 V
- 25. The half life for the decomposition of gaseous compound A is 240 s when the gaseous pressure was 500 Torr initially. When the pressure was 250 Torr, the half life was found to be 4.0 min. The order of the reaction is _____. (Nearest integer)

26. Consider the following metal complexes:

$$[\text{Co(NH}_3)_6]^{3+}$$
 $[\text{CoCl(NH}_3)_5]^{2+}$ $[\text{Co(CN)}_6]^{3-}$ $[\text{Co(NH}_3)_5(\text{H}_2\text{O})]^{3+}$

The spin-only magnetic moment value of the complex that absorbs light with shortest wavelength is _____ B.M. (Nearest integer)

- 27. Among Co³⁺, Ti²⁺, V²⁺ and Cr²⁺ ions, one if used as a reagent cannot liberate H₂ from dilute mineral acid solution, its spin-only magnetic moment in gaseous state is _____ B.M. (Nearest integer)
- 28. While estimating the nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.25 g of the compound neutralized 2.5 mL of 2 M H₂SO₄. The percentage of nitrogen present in organic compound is _____.
- 29. The number of sp^3 hybridised carbons in an acyclic neutral compound with molecular formula C₄H₅N
- **30.** In the given reaction

$$\begin{array}{c|c}
 & O \\
 & H_3C & | \\
 & C - OEt \\
 & CH_2 - C - CH_3 & \hline
 & OEt \\
 & O & OEt
\end{array}$$

(Where Et is $-C_2H_5$)

The number of chiral carbon/s in product A is

SOLUTIONS

- 1. (c): $SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$ *x* mole x mole 2x mole
 - $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$ x mole 2x mole
 - (ii) HCl + NaOH \longrightarrow NaCl + H₂O 2x mole 2x mole

Total number of moles of NaOH required = 4x = 16 $\Rightarrow x = 4.$

- 2. (c): The value of n and l cannot be equal. For any value of n, possible values of l are 0 to n-1.
- 3. (c): In 1 litre of solution, 0.5 mL of HCOOH is present.

Density =
$$\frac{\text{Mass}}{\text{Volume}}$$

Mass of solute =
$$d \times V = 1.05 \text{ g mL}^{-1} \times 0.5 \text{ mL}$$

= 0.525 g

Let mass of solution = 1 kg = 1000 g

Mass of solvent =
$$1000 - 0.525 = 999.475$$
 g

$$\Delta T_f = i \times K_f \times m$$

$$0.0405 = i \times 1.86 \left[\frac{0.525 \times 1000}{46 \times 999.475} \right]$$

(: molar mass of HCOOH = 46 g mol^{-1}) $0.0405 = i \times 0.02124$ or i = 1.9

4. (c):
$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$
No. of millimoles 2 2 - -
initially
No. of millimoles 0 0 2
after reaction

$$[NH_4Cl] = \frac{No. \text{ of millimoles}}{\text{Total volume (in mL)}} = \frac{2}{60} = \frac{1}{30} \text{ M}$$

For salts of strong acid and weak base,

$$pH = \frac{1}{2}[pK_w - pK_b - \log C] = \frac{1}{2}[14 - pK_b - \log C]$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

$$= 7 - \frac{5}{2} - \frac{1}{2}\log\left(\frac{1}{30}\right) \quad [\because pK_b = -\log(1 \times 10^{-5}) = 5]$$

$$= 7 - 2.5 + \frac{1}{2}\log(30) = 7 - 2.5 + \frac{1}{2}[1 + 0.48]$$

$$= 7 - 2.5 + 0.74 = 5.24$$

5. (c): In Haber's process for the preparation of ammonia, catalyst such as iron oxide with small amounts of K₂O and Al₂O₃ is used to increase the rate of attainment of equilibrium.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe_{x}O_{y}} 2NH_{3(g)}$$

$$CO_{(g)} + 3H_{2(g)} \xrightarrow{Ni} CH_{4(g)} + H_{2}O_{(g)}$$

$$CO_{(g)} + H_{2(g)} \xrightarrow{Cu} HCHO_{(g)}$$

$$CO_{(g)} + 2H_{2(g)} \xrightarrow{Cu/ZnO-Cr_{2}O_{3}} CH_{3}OH_{(g)}$$

- (d): IUPAC nomenclature of an element with atomic number 103 is unniltrium, i.e., Lawrencium (Lr) having electronic configuration [Rn] $5f^{14}$ $6d^1$ $7s^2$.
- 7. (d): During the extraction of Cu, the following slag formation reaction takes place.

FeO + SiO₂
$$\longrightarrow$$
 FeSiO₃ Slag

- (a): Reaction of H_2O_2 with MnO_4^- in acidic medium: $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$
- 9. (a): Density (g cm⁻³) 0.53 0.97 0.86 1.53 1.90 Thus, correct order is: Li < K < Na < Rb < Cs

10. (b):
$$2BF_3 + 6NaH \xrightarrow{450 \text{ K}} 2B_2H_6 + 6NaF$$

$$(A)$$
 $B_2H_6 + 2NMe_3 \longrightarrow 2BH_3 \cdot NMe_3$

$$(A) \qquad (B) \text{(Tetrahedral, } sp^3)$$

11. (b):
$$Br_2 + 5F_2 \longrightarrow 2BrF_5$$
 (Excess) (Halate)

12. (c): Classical smog is a mixture of smoke, fog and sulphur dioxide (SO_2) .

Photochemical smog comprises of NO, NO₂ and formaldehyde (HCHO).

13. (d):

For salts of strong acid and weak base,

$$pH = \frac{1}{2}[pK_w - pK_b - \log C] = \frac{1}{2}[14 - pK_b - \log C]$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

$$= 7 - \frac{5}{2} - \frac{1}{2}\log\left(\frac{1}{30}\right) \text{ [:: } pK_b = -\log(1 \times 10^{-5}) = 5]$$

$$= 7 - 2.5 + \frac{1}{2}\log(30) = 7 - 2.5 + \frac{1}{2}[1 + 0.48]$$

$$= 7 - 2.5 + 0.74 = 5.24$$
(c): In Haber's process for the preparation of

Oxidation of 'a', i.e., HCHO produces formic acid which is produced by ants.

17. (a):

$$H_2N$$
 NH_2
 NH_2
 NH_2
 NH_2
 $Melamine$
 NH_2
 NH_2

$$\begin{bmatrix}
HN & NH - CH_2 \\
N & NH
\end{bmatrix}_{n}$$

Melamine formaldehyde polymer

18. (a)

19. (b): Drugs that bind to the receptor site and inhibit its natural functions are called antagonists.

$$\begin{array}{c}
CH_2 - OH \\
| \\
CH - OH
\end{array}$$

$$\begin{array}{c}
CH_2 \\
| \\
CH \\
CH_2 - OH
\end{array}$$

$$\begin{array}{c}
CH_2 \\
| \\
CH_2 \\
CH
\end{array}$$

$$\begin{array}{c}
CH_2 \\
| \\
CHO
\end{array}$$

$$\begin{array}{c}
CHO
\end{array}$$

$$\begin{array}{c}
Propenal \\
(Acrolein)
\end{array}$$

Acrolein has pungent smell instead of fruity odour.

21. (2):
$$N_2$$
: $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
 $(\sigma 2p_z)^2$; Diamagnetic
 N_2^- : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
 $(\sigma 2p_z)^2 (\pi^* 2p_x)^1$; Paramagnetic

$$N_2^+: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$$
 $(\sigma 2p_z)^{1}$; Paramagnetic

 $N_2^{--}: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
 $(\sigma 2p_z)^2 (\pi^* 2p_x^1 = \pi^* 2p_y^1)$; Paramagnetic

 $O_2: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
 $(\pi^* 2p_x^1 = \pi^* 2p_y^1)$; Paramagnetic

 $O_2^+: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
 $(\pi^* 2p_x^1 = \pi^* 2p_y^1)$; Paramagnetic

 $O_2^-: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
 $(\pi^* 2p_x^2 = \pi^* 2p_y^1)$; Paramagnetic

 $O_2^{--}: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
 $(\pi^* 2p_x^2 = \pi^* 2p_y^2)$; Diamagnetic

 $O_2^{--}: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
 $(\pi^* 2p_x^2 = \pi^* 2p_y^2)$; Diamagnetic

22. (104): Let $3C_{(s)} + 4H_{2(g)} \longrightarrow C_3H_{8(g)}$
Given,

 $C_3H_{8(g)} + 5O_2 \longrightarrow 3CO_2 + 4H_2O$
...(i)

 $\Delta H = -2220 \text{ kJ/mol}$
 $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$
...(ii)

 $\Delta H = -393.5 \text{ kJ/mol}$
 $AH = -393.5 \text{ kJ/mol}$
 $AH = -393.5 \text{ kJ/mol}$
...(iii)

 \therefore Eq. (ii) \times 3 + eq. (iii) \times 4 – eq. (i), we get

Hydrogen needs a lot of space. It is the most widespread element in the universe.



...(iii)

 $\Delta H = -285.8 \text{ kJ/mol}$

$$3C_{(s)} + 3O_{2(g)} + 4H_{2(g)} + 2O_{2(g)} - C_3H_{8(g)} - 5O_{2(g)}$$

 $\longrightarrow 3CO_{2(g)} + 4H_2O_{(g)} - 3CO_{2(g)} - 4H_2O_{(g)}$
 $3C_{(s)} + 4H_{2(g)} \longrightarrow C_3H_{8(g)}$
 $\Delta H_r^{\circ} = -393.5 \times 3 - 285.8 \times 4 - (-2220)$
 $= -1180.5 - 1143.2 + 2220$
 $= -103.7 \text{ kJ/mol} \approx -104 \text{ kJ/mol}$

23. (22): Pressure of moist gas = 4 atm Vapour pressure of $H_2O = 0.4$ atm Pressure of dry gas = 4 - 0.4 = 3.6 atm On doubling volume, pressure of gas will change so, $P_1V_1 = P_2V_2 \implies (3.6)V = P_2 \times 2V \implies P_2 = 1.8$ atm But vapour pressure remains the same.

So,
$$P_{\text{total}} = P_{\text{gas}} + (\text{V.P})_{\text{H}_2\text{O}}$$

= 1.8 + 0.4 = 2.2 atm = 22 × 10⁻¹ atm

24. (4): Anode: $[\operatorname{Zn}_{(s)} \longrightarrow \operatorname{Zn}^{2+}_{(aq)} + 2e^{-}] \times x$ Cathode: $[\operatorname{Sn}^{x+} + xe^{-} \longrightarrow \operatorname{Sn}_{(s)}] \times 2$

$$xZn_{(s)} + 2Sn^{x+} \longrightarrow xZn^{2+}_{(aq)} + Sn_{(s)}$$

$$E_{\text{cell}}^{\circ} = E_{\text{Sn}}^{\circ} x_{+/\text{Sn}} - E_{\text{Zn}}^{\circ} 2_{+/\text{Zn}} = 0.008 - (-0.763)$$

= 0.771 V

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.06}{2x} \log \left(\frac{[\text{Zn}^{2+}]^{x}}{[\text{Sn}^{x+}]^{2}} \right)$$

$$0.801 = 0.771 - \frac{0.06}{2x} \log 10^{-2} \quad \text{or} \quad 0.03 = +\frac{0.06}{x}$$

Total number of electrons involved = 2x = 4

25. (1):
$$\frac{(t_{1/2})_I}{(t_{1/2})_{II}} = \left(\frac{P_I}{P_{II}}\right)^{1-n}$$

$$\Rightarrow \left(\frac{240}{4 \times 60}\right) = \left(\frac{500}{250}\right)^{1-n} \Rightarrow 1 = (2)^{1-n}$$

$$\Rightarrow (2)^0 = (2)^{1-n} \Rightarrow 1-n=0$$

$$\therefore n=1$$

26. (0): As strong field ligand causes maximum splitting so, the compound having a strong field ligand absorbs maximum energy *i.e.*, absorbs light with the shortest wavelength.

Order of splitting of the given complexes : $\left[\text{CoCl}(\text{NH}_3)_5 \right]^{2+} < \left[\text{Co}(\text{NH}_3)_5 (\text{H}_2\text{O}) \right]^{3+} < \\ \left[\text{Co}(\text{NH}_3)_6 \right]^{3+} < \left[\text{Co}(\text{CN})_6 \right]^{3-}$

So, the complex that absorbs light with shortest wavelength is $[Co(CN)_6]^{3-}$.

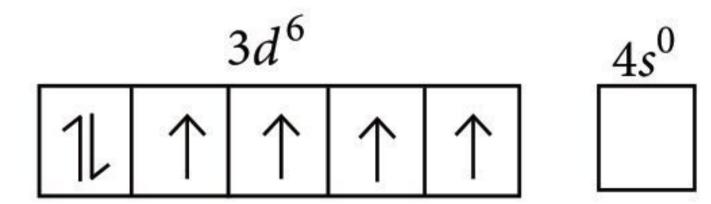
$$_{27}\text{Co}^{3+} = 3d^6 4s^0 \implies t_{2g}^{2,2,2}, e_g^{0,0}$$

Number of unpaired electrons = 0

So,
$$\mu = 0$$

 \therefore x=2

27. (5): On the basis of electrochemical series, $Co^{3+}(3d^6 4s^0)$ being most stable cannot liberate H_2 from dilute mineral acid solution. In gaseous state, its electronic configuration is



i.e.,
$$n = 4$$

$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.89 \approx 5 \text{ B.M}$$

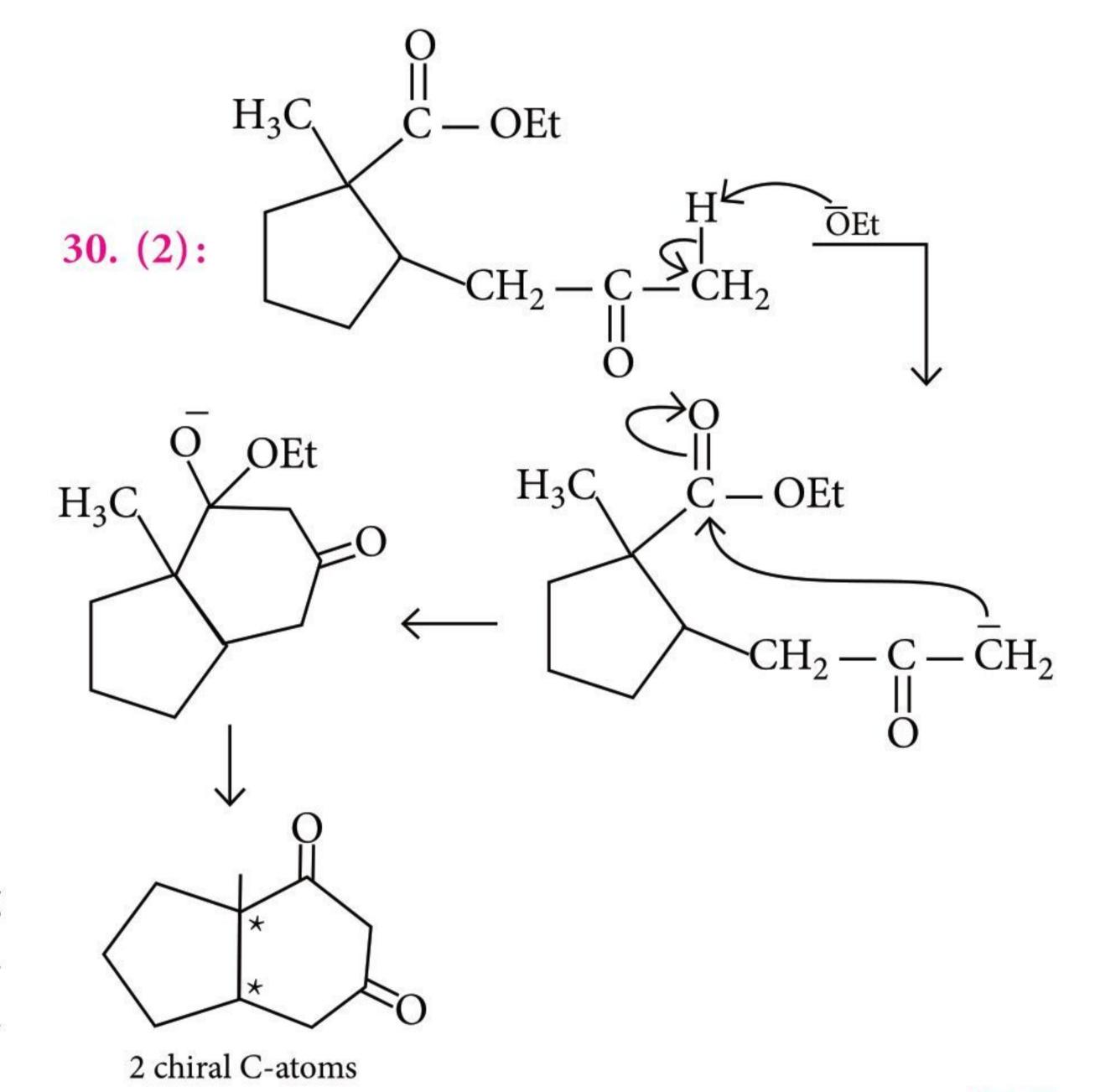
28. (56): Percentage of N =

1.4 × Vol. of acid used × Basicity of acid × Molarity of acid

Mass of substance taken

$$=\frac{1.4\times2.5\times2\times2}{0.25}=56\%$$

29. (1): The possible structure for an acyclic neutral compound, C_4H_5N is $CH_3-CH=CH-C\equiv N$. Thus, only one C-atom is sp^3 -hybridised.



Quotable Quote 99

"I am the master of my failure... If I never fail how will I ever learn."

C.V. Raman

3838



- 1. Temperature coefficient of a reaction is '2'. When temperature is increased from 30°C to 90°C the rate of reaction is increased by
 - (a) 60 times
- (b) 64 times
- (c) 150 times
- (d) 400 times.
- 2. For the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$, the rate is directly proportional to [N₂O₅]. At 45 °C, 90% of the N₂O₅ reacts in 3600 seconds. The value of the rate constant is

 - (a) $3.20 \times 10^{-4} \text{ sec}^{-1}$ (b) $3.20 \times 10^{-3} \text{ sec}^{-1}$

 - (c) $6.40 \times 10^{-4} \text{ sec}^{-1}$ (d) $6.40 \times 10^{-3} \text{ sec}^{-1}$
- In which of the following arrangements, the order is not according to the property indicated against it?
 - (a) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ increasing atomic size

(b) B < C < N < O increasing first ionization

energy

- (c) I < Br < F < Cl
- increasing electron gain enthalpy
- (d) Li < Na < K < Rb increasing metallic radii
- 4. The ionic product of Ni(OH)₂ is 2.0×10^{-15} . The molar solubility of Ni(OH)₂ in 0.10 M NaOH is
 - (a) 2.0×10^{-13}
- (b) 2.0×10^{-14}
- (c) 1.0×10^{-13}
- (d) 1.0×10^{-14}
- 5. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are -890.3 kJ mol⁻¹, $-393.5 \text{ kJ mol}^{-1} \text{ and } -285.8 \text{ kJ mol}^{-1} \text{ respectively.}$ Enthalpy of formation of $CH_{4(g)}$ will be
 - (a) $-74.8 \text{ kJ mol}^{-1}$
- (b) $-52.27 \text{ kJ mol}^{-1}$
- (c) $+74.8 \text{ kJ mol}^{-1}$
- (d) $+52.26 \text{ kJ mol}^{-1}$
- 6. Crystal field stabilisation energy for high spin d^4 octahedral complex is
 - (a) $-1.2 \Delta_0$
- (b) $-0.6 \, \Delta_0$
- (c) $-1.8 \Delta_0$
- (d) $-1.6 \Delta_0 + P$
- 7. The mass of carbon present in 0.5 mole of $K_4[Fe(CN)_6]$ is

 - (a) 1.8 g (b) 18 g (c) 3.6 g (d) 36 g

- According to kinetic theory of gases, a gas molecule travels between two successive collisions
 - (a) in circular path
 - (b) in a wavy path
 - (c) in a straight line path
 - (d) with an accelerated velocity.
- The value of van der Waals' constant 'a' for gases O₂, N₂, NH₃ and CH₄ are 1.360, 4.170 and $2.253 L^2$ atm mol⁻² respectively. The gas which can be most easily liquefied is
- (a) O_2 (b) N_2 (c) NH_3
- 10. Camphor is often used in molecular mass determination because
 - (a) it has a very high cryoscopic constant
 - (b) it is volatile
 - (c) it is solvent for organic substances
 - (d) it is readily available.
- 11. Fe₃O₄ is ferrimagnetic at room temperature but at 850 K it becomes
 - (a) diamagnetic
- (b) paramagnetic
- (c) ferromagnetic
- (d) non-magnetic.
- **12.** To get *n*-type semiconductor, the impurity to be added to Si should have the following number of valence electrons
 - (a) 1
- (b) 2
- (c) 3
- (d) 5
- 13. Poling process is used
 - (a) for removal of Cu₂O from Cu
 - (b) for removal of Al₂O₃ from Al
 - (c) for removal of Fe₂O₃ from Fe
 - (d) for removal of Cu₂O from Cu₂O₂.
- 14. A gas present in a cylinder filled with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litres to a volume of 6 litres. In doing so it absorbs 800 J heat from surroundings. Determine increase in internal energy of process.
 - (a) 405.04 J
- (b) 96.81 J
- (c) 394.95 J
- (d) 1205.04 J

- 15. Which statement is FALSE?
 - (a) van der Waals' constant 'a' is measure of magnitude of intermolecular attractive force within the gas.
 - (b) At low temperature intermolecular attraction is more significant and van der Waals' constant 'a' is high at low temperature.
 - (c) van der Waals' constant 'a' is independent of the pressure of the gas.
 - (d) van der Waals' gas approximates ideal gas behavior when pressure approaches zero.
- 16. The resistance of a 0.1 N solution of salt is found to be 2.5×10^3 ohms. Calculate the equivalent conductance of the solution.

(Cell constant = 1.15 cm^{-1})

- (a) $2.30 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}$
- (b) $4.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}$
- (c) $5.23 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}$
- (d) $0.98 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}$
- 17. Borazine is
 - (a) $B_3N_3H_6$
- (b) B_2H_6
- (c) $B_2N_3H_6$
- (d) $B_3N_2H_6$
- 18. When sodium is dissolved in liquid NH₃, a solution of deep blue colour is formed. The colour of the solution is due to
 - (a) ammoniated electron
 - (b) sodium ion
 - (c) sodium amide
 - (d) ammoniated sodium ion.
- 19. The respective number of bridging 'CO' groups in $[Co_2(CO)_8]$ and $[Mn_2(CO)_{10}]$ is/are
 - (a) 2, 0
- (b) 1, 0 (c) 0, 1
- 20. One mole of PdCl₂·4NH₃ upon reaction with excess of AgNO₃ gives two moles of AgCl. The coordination number of complex formed will be
 - (a) two
- (b) four (c) six
- (d) three.
- 21. The correct electron gain enthalpy trend is
 - (a) O < S < Se < Te < Po
 - (b) O < S > Se > Te > Po
 - (c) O > S > Se > Te > Po
 - (d) O < S > Se < Te > Po
- 22. MnO₄ is tetrahedral in geometry. There is π bonding between Mn and oxygen by the overlap of
 - (a) *p-p* orbitals
- (b) *s-p* orbitals
- (c) *p-d* orbitals
- (d) *s-d* orbitals.
- 23. The highest magnetic moment among the following coordinated compound is shown by

- (b) $[Fe(H_2O)_6]^{2+}$
- (c) $K_2[MnCl_4]$

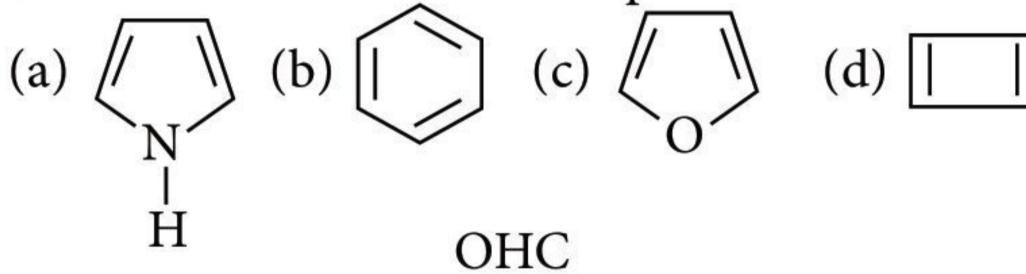
(a) $K_4[Mn(CN)_6]$

- (d) $Ni(CO)_4$
- 24. The transition metal oxides or halides does not exist among the following is
 - (a) V_2O_5 (b) MnF_5 (c) CrF_6
- (d) Mn_2O_7
- 25. Acidity of diprotic acids in aqueous solution increases in the order
 - (a) $H_2S < H_2Se < H_2Te$ (b) $H_2Se < H_2S < H_2Te$
 - (c) $H_2\text{Te} < H_2\text{S} < H_2\text{Se}$ (d) $H_2\text{Se} < H_2\text{Te} < H_2\text{S}$
- 26. The commercial name of "Calgon" is
 - (a) sodium aluminium silicate
 - (b) peroxodisulphate
 - (c) sodium sulphate decahydrate
 - (d) sodium hexametaphosphate.
- 27. The correct order of an arrangement of the group 14 elements with decrease in their first ionisation enthalpy is
 - (a) C > Si > Ge > Sn > Pb
 - (b) C > Si > Ge > Pb > Sn
 - (c) C > Si > Sn > Ge > Pb
 - (d) C > Si > Pb > Sn > Ge
- 28. Which of the following oxoacids of phosphorus contains four P — OH bonds?
 - (a) Orthophosphoric acid
 - (b) Metaphosphoric acid
 - (c) Hypophosphoric acid
 - (d) Hypophosphorous acid
- 29. Which one is used for titration with KMnO₄ in acidic medium?
 - - (b) H_2SO_4 (c) HNO_3 (d) $HClO_4$
- 30. When manganese dioxide is fused with KOH or K₂CO₃ in air, it gives
 - (a) potassium manganate
 - (b) potassium permanganate
 - (c) manganese heptoxide
 - (d) manganese oxide.
- 31. Which of the following alkaline earth metals have strong tendency towards the formation of metal chloride hydrates?
 - (a) BaCl₂
- (b) MgCl₂
- (c) CaCl₂
- (d) SrCl₂
- **32.** Which one of the following molecules is formed by *p-p* overlapping?
 - (a) HCl
- (b) Cl₂
- (c) H_2O
- (d) NH₃
- **33.** Gadolinium belongs to 4*f* series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?

- (a) $[Xe]4f^75d^16s^2$ (b) $[Xe]4f^65d^26s^2$ (c) $[Xe]4f^86d^2$ (d) $[Xe]4f^95s^1$

- 34. The product in the following reaction is

- COOH (a) COOH
- COOH (b) CH₂OH
- \checkmark OH
- 35. In the polysaccharides, the monosaccharides are linked to each other by
 - (a) glycosidic linkage (b) peptide linkage
 - (c) nucleosidic linkage (d) hydrogen bonding.
- **36.** Select the non-aromatic compound.



- 37. The IUPAC name of
 - (a) 2-methyl-3-bromohexanal
 - (b) 2-methyl-3-bromobutanal
 - (c) 3-bromo-2-methylbutanal
 - (d) 3-bromo-2-methylpentanal.
- 38. The human body does not produce

 - (a) vitamins (b) enzymes
 - (c) proteins
- (d) hormones.

Ph
$$CH - O - C - Ph + aq. HI \longrightarrow X. X will be Ph$$

- Ph\
 (a) Ph C I(b) Ph C OHPh\
 Ph\
- Ph CH I (d) Ph CH OH Ph
- **40.** Tincture of iodine is
 - (a) aqueous solution of I_2 + ether
 - (b) alcoholic solution of I_2 + water
 - (c) solution of I₂ in aqueous KI
 - (d) aqueous solution of KI.
- 41. During the following sequence of reactions:

Phenol
$$\xrightarrow{\text{NaOH}} A \xrightarrow{\text{(i) CO}_2} B$$

The main product *B* formed is

- (a) salicylic acid
- (b) salicylaldehyde
- (c) benzoquinone
- (d) aspirin.

- 42. Which of the following reacts with phenol to give Bakelite?
 - (a) HCHO
- (b) CH₃CHO
- (c) $(CH_2CHO)_2$
- (d) CH₃COCH₃
- 43. Which of the following alkyl halides is hydrolysed by S_N 2 mechanism?
 - (a) $C_6H_5CH_2Br$
- (b) CH₃Br
- (c) $H_2C = CHCH_2Br$
- (d) $(CH_3)_3CBr$
- 44. In the reaction

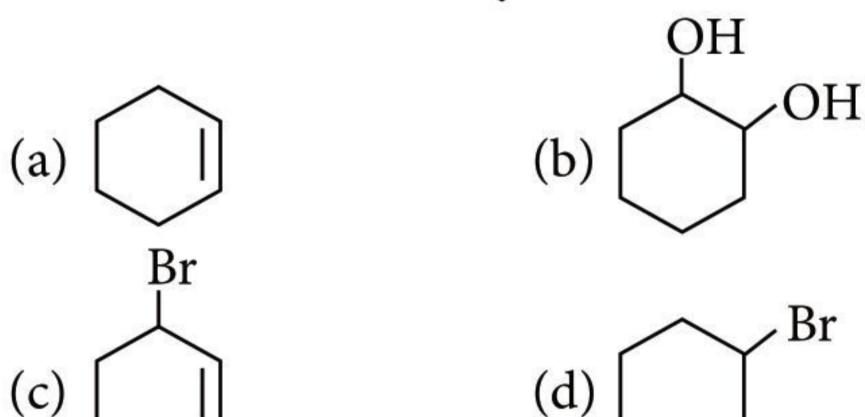
$$CH_3 - C \equiv C - CH_3 \xrightarrow{\text{(i) } X} \xrightarrow{\text{(ii) } H_2O/Zn}$$

$$CH_3 - C = C - CH_3 \xrightarrow{\text{(ii) } H_2O/Zn}$$

X will be:

- (a) HNO_3
- (b) O₂
- (c) O_3
- (d) KMnO₄
- 45. 3-Phenyl propene on reaction with HBr gives (as a major product)
 - (a) $C_6H_5 CH_2CH(Br)CH_2Br$
 - (b) $C_6H_5CH(Br)CH_2CH_3$
 - (c) $C_6H_5 CH_2CH_2CH_2Br$
 - (d) $C_6H_5 CH(Br)CH = CH_2$

46. Predict the product
$$\frac{OH}{\frac{1. PBr_3}{2. alc. KOH}}$$
?



- 47. How many chiral centres are present in natural penicillin?
 - (a) 3
- (b) 4 (c) 5
- (d) 6
- 48. Which one of the following pairs is not correctly matched?
 - (a) $C = O \longrightarrow CH_2$ Clemmensen reduction
 - (b) $C = O \longrightarrow CHOH$ Wolff-Kishner reduction
 - (c) $-\ddot{C} Cl \longrightarrow -CHO$ Rosenmund reduction
 - (d) $-C \equiv N \longrightarrow -CHO$ Stephen reduction
- 49. Name the reaction given below:

$$CH_3 - Br + AgF \longrightarrow CH_3F + AgBr$$

- (a) Finkelstein reaction (b) Swarts reaction
- (c) Etard reaction
- (d) Wurtz reaction

- 50. Pick-out the correct relationship:
 - (a) Antibiotics → Bacterial infection → Ranitidine
 - (b) Antipyretics → Reduce body temperature → Paracetamol
 - (c) Antiseptics → Wound infection → Saccharin
 - (d) Tranquilizers \rightarrow Psychotherapeutic agent \rightarrow Phenolphthalein

SOLUTIONS

1. **(b)** :
$$\frac{K_T + 10}{K_T} = 2$$
 (given)

In going from 30 °C to 90 °C, total change in temperature is 60 °C.

So, rate of reaction will be increased by 2^6 times *i.e.*, 64 times.

2. (c) : Given, $2N_2O_5 \longrightarrow 4NO_2 + O_2$

 $r \propto [N_2O_5]$ *i.e.*, first order.

For first order reactions,

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{3600 \text{ sec}} \log \frac{100}{10} = 6.4 \times 10^{-4} \text{ sec}^{-1}$$

- 3. (b) : The correct increasing order of first ionization energy is B < C < O < N, N has higher ionization energy than O due to extra stability of half filled *p*-orbital electronic configuration (N : $1s^2 2s^2 2p^3$).
- 4. (a): Let the solubility of Ni(OH)₂ = S Ni(OH)₂ \rightleftharpoons Ni²⁺ + 2OH⁻ S 2S

The total concentration of $OH^- = (0.10 + 2S) \text{ mol/L}$ because the solution already contain 0.10 mol/L of OH^- from NaOH

$$K_{sp} = [\text{Ni}^{2+}] [\text{OH}^-]^2 \Rightarrow [\text{S}] [2S + 0.10]^2$$

$$\therefore$$
 2S <<< 0.10 thus 2S + 0.10 \approx 0.10

$$2.0 \times 10^{-15} = [S] [0.10]^2$$

 $S = 2.0 \times 10^{-13}$

Therefore, molar solubility of $[Ni^{2+}]$ is 2.0×10^{-13} .

5. (a) : Given; (i) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$; $\Delta H = -890.3 \text{ kJ/mol}$

(ii)
$$C_{(s)} + O_{2(g)} \rightarrow CO_2$$
; $\Delta H = -393.5$ kJ/mol

(iii)
$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2 O_{(g)}$$
; $\Delta H = -285.8 \text{ kJ/mol}$

or
$$2H_2 + O_2 \rightarrow 2H_2O$$
; $\Delta H = -571.6 \text{ kJ}$

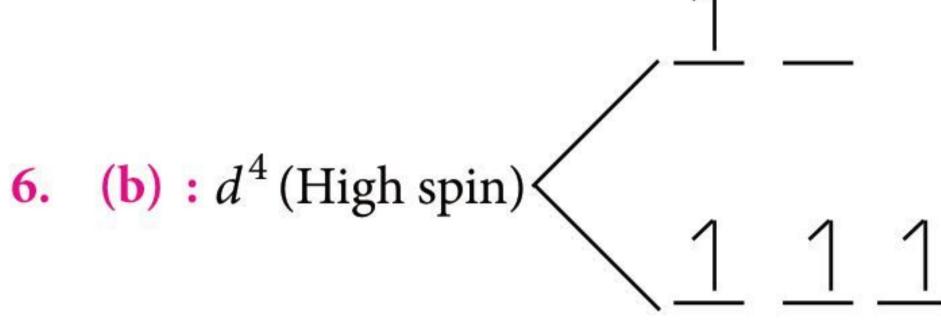
On adding equations (ii) and (iii) and subtracting equation (i) we get,

$$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$$

$$\Delta H = -393.5 - 571.6 + 890.3 = -74.8 \text{ kJ/mol}$$

 \therefore Enthalpy of formation of CH₄ is -74.8 kJ/mol.

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e.g., CFSE = $[3 \times (-0.4) + 1 \times (0.6)] \Delta_0 = -0.6 \Delta_0$

- 7. (d): 0.5 mole of $K_4[Fe(CN)_6]$ have 3 moles of C. Mass of 3 moles of carbon = $3 \times 12 = 36$ g
- 8. (c): A gas molecule travels in a straight line path between two successive collisions.
- 9. (c): Gas having high value of *a* will be liquefied more easily. van der Waals' constant '*a*' represents the magnitude of intermolecular forces of attraction between gas molecules.

Note: Value of 'a' for N₂ is not given in the question which is 1.40.

- 10. (a): Camphor basically has a very high cryoscopic constant due to which the depression in freezing point will be more and the accuracy in measurement of molecular mass will be greater.
- 11. (b): Fe_3O_4 is ferrimagnetic and it gets converted to paramagnetic on heating.
- **12.** (d): Silicon on dopping with elements having higher valence electrons gives *n*-type semiconductor.
- 13. (a) : Poling method is employed in the purification of Cu which contains CuO and Cu₂O as impurities.

14. (c) :
$$\Delta U = q + w$$

$$w = -P(\Delta V) = -1 \times (6 - 2) = -4 \text{ L atm}$$

$$4 \text{ L-atm} = 4 \times 101.325 \text{ J} = 405.3 \text{ J}$$

$$\Delta U = q + w = 800 \text{ J} - 405.3 \text{ J} = 394.7 \text{ J}$$

15. (b): van der Waals' constant 'a' depends only on the nature of the gas.

16. (b) :
$$\Lambda_{eq} = \frac{\kappa}{c} \times 1000$$

$$\kappa = \frac{1}{R} \times G^* = \frac{1.15 \text{ cm}^{-1}}{2.5 \times 10^3 \Omega} = 0.46 \times 10^{-3} \text{ cm}^{-1} \Omega^{-1}$$

$$\Lambda_{eq} = \frac{0.46 \times 10^{-3}}{0.1} \times 1000 = 4.6 \ \Omega^{-1} \ \text{cm}^2 \ \text{eq}^{-1}$$

- 17. (a): B₃N₃H₆ is borazine, which is known as inorganic benzene.
- 18. (a) : Na + $(x+y)NH_3 \rightarrow [Na(NH_3)_x]^+ + [e(NH_3)_y]^-$

It has 2 bridging CO groups.

$$\begin{array}{c|c} CO_{CO}CO\\ CO / CO\\ OC - Mn - Mn / CO\\ OC / CO / CO\\ \end{array}$$

It has no bridging CO groups.

20. (b): The complex is $[Pd(NH_3)_4]Cl_2$

 $[Pd(NH_3)_4] Cl_2 \rightleftharpoons [Pd(NH_3)_4]^{2+} + 2Cl^{-}$

Hence two moles of Cl⁻ are precipitated by excess AgNO₃ as AgCl. So coordination number of complex is 4.

21. (b): Generally in a group, electron gain enthalpy decreases while going down but oxygen has less electron gain enthalpy than sulphur because of small size and high electronic repulsion.

22. (c):
$$O \\ | M_n \\ O^-$$

 π -Bonding between oxygen and manganese takes place due to overlapping of *p-d* orbitals.

23. (c) : In $K_2[MnCl_4]$: Mn is in + 2 O.S and Cl⁻ is a weak field ligand.

 $Mn^{2+}: d^5$

 Mn^{2+} in $[\mathrm{MnCl_4}]^{2-}$: $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$. It has five unpaired electrons hence has maximum magnetic moment.

24. (b): The highest fluoride of Mn is MnF₄. MnF₅ is not stable hence, does not exist.

Scientist of the Month

Jacobus Henricus van 't Hoff

Early Life and Education

Jacobus Henricus "Henry" van't Hoff Jr. was a Dutch physical chemist. A highly influential theoretical chemist of his time, Van't Hoff was the first winner of the Nobel Prize in Chemistry. His pioneering work helped find the modern theory of chemical affinity, chemical equilibrium, chemical kinetics, and chemical thermodynamics. In his pamphlet, Van't Hoff formulated



Jacobus Henricus van 't Hoff (30 August 1852 - 1 March 1911)

the theory of the tetrahedral carbon atom and laid the foundations of stereochemistry. In 1875, he predicted the correct structures of allenes and cumulenes as well as the axial chirality. He is also widely considered one of the founders of physical chemistry as the discipline is known today.

- The third of seven siblings, Van't Hoff was born in Rotterdam, Netherlands on 30 August 1852. His father was Jacobus Henricus van't Hoff Sr., a physician, and his mother was Alida Kolff van't Hoff. From a young age, he was interested in science and nature, and frequently took part in botanical excursions. In his early years, he showed a strong interest in poetry and philosophy. He considered Lord Byron to be his idol.
- Against the wishes of his father, Van't Hoff chose to study chemistry. First, he enrolled at Delft University of Technology in September 1869, and studied until 1871 and obtained a degree of chemical technologist. He passed all his courses in two years, although the time assigned to study was three years. Then he enrolled at University of Leiden to study chemistry. He then studied in Bonn, Germany, with August Kekulé and in Paris with Adolphe Wurtz. He received his doctorate under Eduard Mulder at the University of Utrecht in 1874.

Work

- Van't Hoff earned his earliest reputation in the field of organic chemistry. In 1874, he accounted for the phenomenon of optical activity by assuming that the chemical bonds between carbon atoms and their neighbours were directed towards the corners of a regular tetrahedron. This three-dimensional structure accounted for the isomers found in nature.
- Three months before his doctoral degree was awarded, Van't Hoff published this theory, which today is regarded as the foundation of stereochemistry.
- In 1884, Van't Hoff published his research on chemical kinetics in which he described a new method for determining the order of a reaction using graphics and applied the laws of thermodynamics to chemical equilibria. He also introduced the modern concept of chemical affinity.

Honours and Awards

- In 1885, Van't Hoff was appointed as a Member of the Royal Netherlands Academy of Arts and Sciences.
- In 1904, he was elected as a member of the American Philosophical Society.
- He was awarded the Davy Medal of the Royal Society in 1893 (along with Le Bel), and elected a Foreign Member of the Royal Society (ForMemRS) in 1897.
- He was awarded the Helmholtz Medal of the Prussian Academy of Sciences (1911), and appointed Knight of the French Legion of Honour (1894) and Senator in the Kaiser-Wilhelm-Gesellschaft (1911).
- Van't Hoff became an Honorary Member of the British Chemical Society in London, the Royal Netherlands Academy of Arts and Sciences (1892), American Chemical Society (1898), the Académie des Sciences in Paris (1905), and the Netherlands Chemical Society (1908).
- Of his numerous distinctions, Van't Hoff regarded winning the first Nobel Prize in Chemistry as the culmination of his career. The following are named after him:
 - Van't Hoff factor, Van't Hoff equation and Le Bel-Van't Hoff rule
- On 14 May 2021, asteroid 34978 Van't Hoff, discovered by astronomers with the Palomar–Leiden survey in 1977, was named in his memory.

25. (a): Acidic strength increases from H_2S to H_2Te , due to decrease in the bond enthalpy from H_2S to H_2Te .

26. (d) : Calgon is sodium hexametaphosphate $(Na_6P_6O_{18})$.

27. (b) : Decreasing order of first ionisation enthalpy is C > Si > Ge > Pb > Sn.

Pb has greater first ionisation enthalpy than Sn because of poor shielding effect of intervening *d* and *f* orbitals and increase in size of the atom.

28. (c): Hypophosphoric acid

It has 4 (P — OH) bonds.

29. (b) : $KMnO_4$ is a strong oxidising agent, so H_2SO_4 is used in titration with $KMnO_4$.

30. (a) :
$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

Potassium manganate

31. (b) : MgCl₂ is deliquescent and crystallise to form MgCl₂·8H₂O.

32. (b) : Cl_2 molecule is formed by p-p overlapping.

33. (a)

34. (b): It is an intramolecular Cannizzaro reaction.

$$\begin{array}{c|c}
CHO & \xrightarrow{1. \text{ Conc. NaOH}} & \xrightarrow{COOH} \\
CHO & \xrightarrow{2. \text{ H}_2\text{O/H}^+} & \xrightarrow{CH_2\text{OH}}
\end{array}$$

35. (a): In polysaccharides, monosaccharides are linked by glycosidic linkage.

36. (d) : It is a non-aromatic compound as it does not follow Huckel $(4n + 2)\pi$ electron rule. Since it contains 4π electrons it is an anti-aromatic compound.

3-Bromo-2-methylpentanal

38. (a): Human body does not produce vitamins.

39. (a, d):
$$Ph$$

$$CH - O - C - Ph$$

$$Ph + aq.HI \xrightarrow{S_N 1}$$

$$Ph - C - I + Ph$$

$$Ph - C - I + CH - OH$$

(Ph)₃C⁺ carbocation formed is more stable.

40. (b)

OH ONa OH

NaOH (i)
$$CO_2$$
 (ii) H^+ (B)

Salicylic acid

42. (a) : Phenol and formaldehyde in the presence of either an acid or a base catalyst form novolac. Novolac on heating with formaldehyde form bakelite.

43. (b) : CH_3Br undergoes hydrolysis by S_N2 mechanism due to less steric hindrance.

44. (c): It is an example of ozonolysis reaction of alkyne.

$$CH_{3}-C \equiv C-CH_{3} \xrightarrow{O_{3}} CH_{3}-C \xrightarrow{C} C-CH_{3}$$

$$CH_{3}-C-C-CH_{3} \xleftarrow{Zn/H_{2}O}$$

$$CH_{3}-C-C-CH_{3} \xleftarrow{Zn/H_{2}O}$$

45. (b):
$$CH_2 - CH = CH_2 \xrightarrow{H^+}$$

$$CH_2 - CH - CH_3 \xrightarrow{1, 2 - H^+ \text{shift}}$$

(Less stable)

$$\overset{+}{CH} - CH_2 - CH_3 \xrightarrow{Br^-} CH(Br) CH_2CH_3$$
(More stable due to resonance)

46. (a) :
$$PBr_3$$
 $Alc.KOH$

48. (b):
$$C = O \xrightarrow{NH_2NH_2} CH_2$$
 (Wolff-Kishner reduction)

49. (b)

50. (b): Paracetamol is an analgesic as well as antipyretic.

CHAPTERWISE PRACTICE PAPER 2023

CUET (UG)

SERIES - Solid State | Solutions

Section II of CUET (UG) is domain specific. In this section of Chemistry 40 questions to be attempted out of 50.

Time Allowed: 45 Minutes Maximum Marks: 200

Multiple Choice Questions (MCQs)

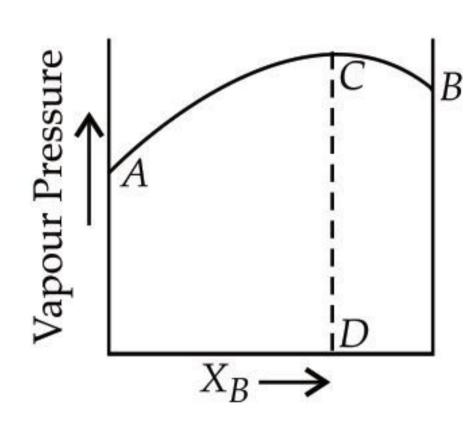
- Which of the following does not represent a type of crystal system?
 - (a) Triclinic
- (b) Monoclinic
- (c) Rhombohedral
- (d) Isotropical
- Which of the following is a colligative property?
 - (a) Lowering of vapour pressure
 - (b) Osmotic pressure
 - (c) Boiling point
- (d) Change in entropy
- 3. If three elements X, Y and Z crystallise in a ccplattice with X atoms at the corners, Y atoms at the cube centre and Z atoms at the edges, the formula of the compound will be
 - (a) *XYZ*
- (b) XYZ_2
- (c) XYZ_3
- (d) X_2Y_2Z
- 4. 18 g glucose $(C_6H_{12}O_6)$ is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is
 - (a) 7.6
- (b) 76.0
- (c) 752.4
- (d) 759.0
- Monoclinic sulphur is an example of monoclinic crystal system. What are the characteristics of the crystal system?
 - (a) $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^{\circ}$
 - (b) $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$
 - (c) $a = b \neq c$, $\alpha = \beta = \gamma = 90^{\circ}$
 - (d) $a \neq b \neq c$, $\alpha = \gamma = 90^{\circ}$, $\beta \neq 90^{\circ}$
- 5.5 mg of nitrogen gas dissolves in 180 g of water at 273 K and one atm pressure due to nitrogen gas. The mole fraction of nitrogen in 180 g of water at 5 atm nitrogen pressure is approximately
 - (a) 1×10^{-6}
- (b) 1×10^{-5}
- (c) 1×10^{-3}
- (d) 1×10^{-4}
- 7. How many chloride ions are surrounding sodium ion in sodium chloride crystal?
 - (a) 4
- (b) 8
- (c) 6
- (d) 12

- On mixing 20 mL of acetone with 60 mL of chloroform, the total volume of the solution is
 - (a) less than 80 mL
- (b) more than 80 mL
- (c) equal to 80 mL
- (d) unpredictable.
- The edge length of sodium chloride unit cell is 564 pm. If the size of Cl ion is 181 pm. The size of Na⁺ ion will be
 - (a) 101 pm (b) 181 pm (c) 410 pm (d) 202 pm
- 10. Which of the following will show a negative deviation from Raoult's law?
 - (a) Acetone-benzene
- (b) Acetone-ethanol
- (c) Benzene-methanol (d) Acetone-chloroform
- 11. Crystalline CsCl has density 3.988 g cm⁻³. The volume occupied by single CsCl ion pair in the crystal will be
 - (a) $7.010 \times 10^{-3} \text{ cm}^3$
- (b) $7.010 \times 10^{-23} \text{ cm}^3$
- (c) $1.014 \times 10^{-3} \text{ cm}^3$
- (d) $1.542 \times 10^{-5} \text{ cm}^3$
- 12. When the pure solvent diffuses out of the solution through the semipermeable membrane then the process is called
 - (a) sorption
- (b) dialysis
- (c) osmosis
- (d) reverse osmosis.
- 13. Which of the following will have metal deficiency defect?
 - (a) NaCl
- (b) FeO
 - (c) KCl
- (d) ZnO
- 14. The relative lowering in vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of the solute. This statement is called
 - (a) Henry's Law
- (b) Raoult's law
- (c) Knonwaloff's rule
- (d) Lever rule.
- 15. Paramagnetic substances are magnetised in a magnetic field in the same direction. Paramagnetism is due to the presence of

- (a) one or more unpaired electrons
- (b) all paired electrons
- (c) permanent spin and orbital motion
- (d) parallel and anti-parallel spins in equal number.
- 16. Which one of the following is correct at freezing point.
 - (a) Solid and liquid have non-identical vapour pressure.
 - (b) Solid and liquid are in equilibrium.
 - (c) Vapour pressure of liquid is greater than that of solid.
 - (d) None of these
- 17. The yellow colour of ZnO and conducting nature produced upon heating is due to
 - (a) metal excess defects due to interstitial cation
 - (b) extra positive ions present in an interstitial site
 - (c) trapped electrons
 - (d) all of these.
- 18. Which of the following aqueous solutions has highest freezing point?

 - (a) $0.1 \text{ molal Al}_2(SO_4)_3$ (b) 0.1 molal BaCl_2
 - (c) 0.1 molal AlCl₃
- (d) 0.1 molal NH₄Cl
- 19. The coordination number of an atom in the simple cubic unit cell in a crystal lattice is
 - (a) 3
- (b) 2
- (c) 4
- (d) 6
- **20.** The van't Hoff factor 'i' accounts for
 - (a) extent of dissolution of solute
 - (b) extent of dissociation of solute
 - (c) extent of mobility of solute
 - (d) extent of solubility of solute.
- 21. The edge length of the unit cell of NaCl crystal lattice is 5.623 Å and density is 2.16 g cm⁻³ and the molar mass of NaCl is 58.5 g mol⁻¹. The number of moles per unit cell is
 - (a) 4
- (b) 3
- (c) 1
- (d) 2
- 22. A solution of 1.25 g of P in 50 g of water lowers freezing point by 0.3° C. Molar mass of P is 94. $K_{f(\text{water})} = 1.86 \text{ K kg mol}^{-1}$. The degree of association of *P* in water is
 - (a) 80%
- (b) 60%
- (c) 65%
- (d) 75%
- 23. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride?
 - (a) 1.2 g/cm^3
- (b) 2.16 g/cm^3
- (c) 3.64 g/cm^3
- (d) 4.56 g/cm^3

24. The diagram given below is a vapour pressurecomposition diagram for a binary solution of A and B.



In the solution, A—B interactions are

- (a) similar to A A and B B interactions
- (b) greater than A A and B B interactions
- (c) smaller than A A and B B interactions
- (d) unpredictable.
- 25. A semiconductor of Ge can be made p-type by adding
 - (a) trivalent impurity
 - (b) tetravalent impurity
 - (c) pentavalent impurity
 - (d) divalent impurity.
- 26. Benzoic acid undergoes dimerisation in benzene solution, the van't Hoff factor 'i' is related to the degree of association 'x' of the acid as

 - (a) i = (1 x) (b) i = (1 + x)
 - (c) i = (1 x/2) (d) i = (1 + x/2)
- 27. Ionic solids with Schottky defects contain in their structure
 - (a) equal number of cation and anion vacancies
 - (b) interstitial anions and anion vacancies
 - (c) cation vacancies only
 - (d) cation vacancies and interstitial cations.
- 28. If an equimolar solution of CaCl₂ and AlCl₃ in water have boiling point of T_1 and T_2 respectively then
 - (a) $T_1 > T_2$ (b) $T_2 > T_1$ (c) $T_1 = T_2$ (d) $T_1 \neq T_2$
- 29. For an octahedral arrangement the lowest radius ratio limit is
 - (a) 0.155
- (b) 0.732
- - (c) 0.414
- (d) 0.225
- 30. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is
 - (a) 1.14 mol kg^{-1} (b) 3.28 mol kg^{-1}
- - (c) 2.28 mol kg^{-1} (d) 0.44 mol kg^{-1}
- 31. A compound formed by elements A and Bcrystallises in cubic structure in which A atoms are at the corners of the cube while B atoms are at the centre of cube. Formula of the compound is
 - (a) A_2B_3 (b) AB_2
- (c) AB_3
- (d) *AB*



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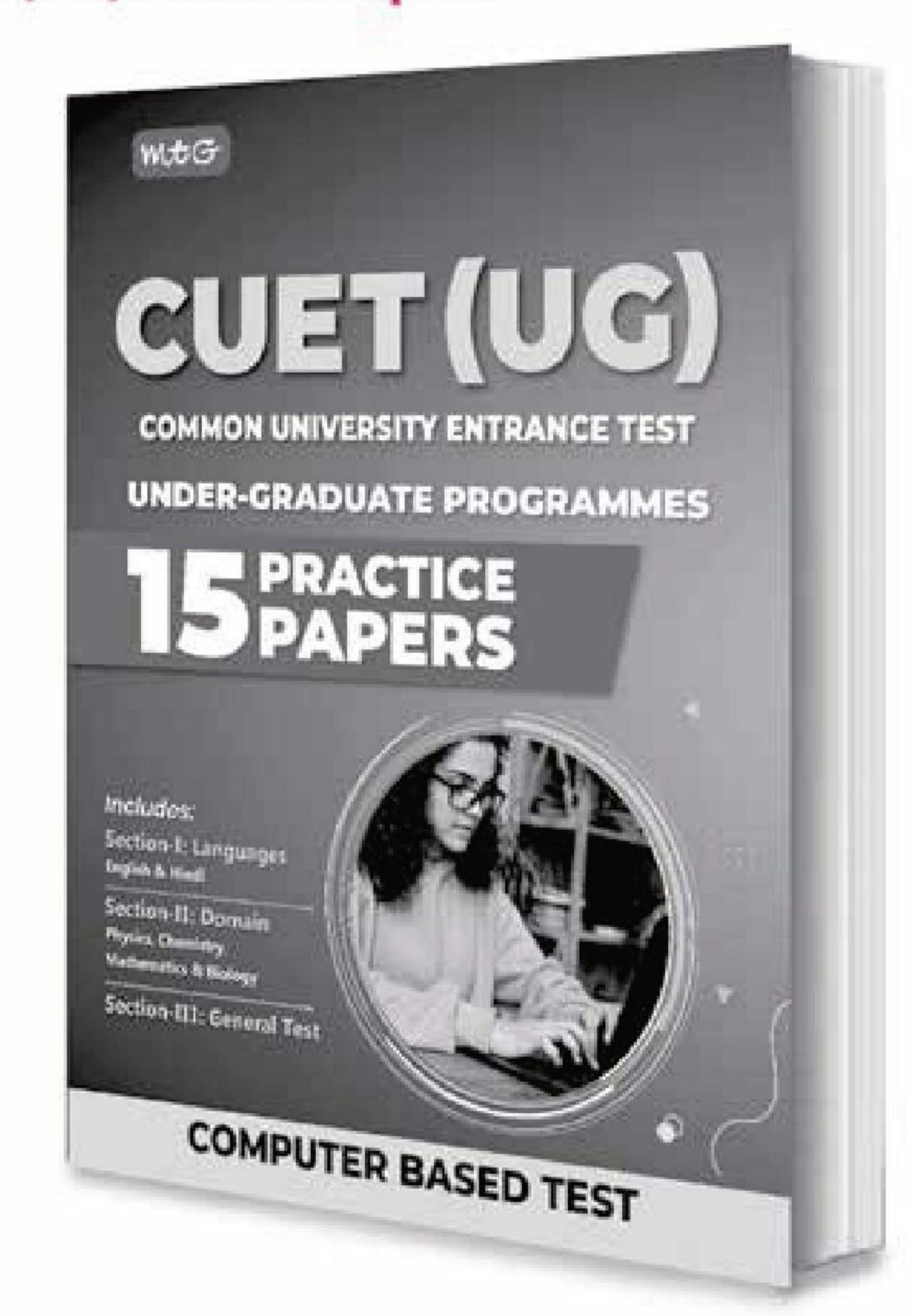
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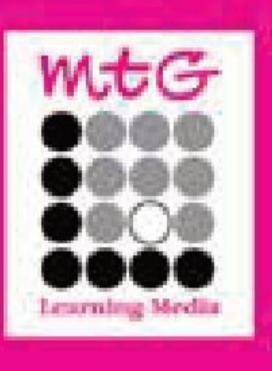
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- 32. Vapour pressure of pure A = 100 torr, moles = 2, vapour pressure of pure B = 80 torr, moles = 3 Total vapour pressure of mixture is
 - (a) 440 torr (b) 460 torr (c) 180 torr (d) 88 torr.
- 33. What type of crystal defect is shown in the given figure? Na^+ $Cl^ Na^+$ $Cl^ Na^+$
 - (a) Frenkel defect $Cl^- \square Cl^- Na^+ Cl^-$
 - (b) Schottky defect Na^+ $Cl^ Na^+$ \square Na^+
 - (c) Interstitial defect $Cl^ Na^+$ \square Na^+ Cl^-
 - (d) Cation excess defect Na⁺ Cl⁻ Na⁺ Cl⁻ D
- 34. The molar freezing point constant for water is 1.86 °C/m. If 342 g of cane sugar ($C_{12}H_{22}O_{11}$) is dissolved in 1000 g of water, the solution will freeze at
 - (a) -1.86 °C
- (b) 1.86 °C
- (c) -3.92 °C
- (d) 2.42 °C

Assertion & Reason Based MCQs

For question numbers 35-38, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) If both assertion and reason are correct and reason is the correct explanation of assertion.
- (b) If both assertion and reason are correct but reason is not the correct explanation of assertion.
- (c) If assertion is correct but reason is wrong.
- (d) If assertion is wrong but reason is correct.
- **35. Assertion :** Glass panes fixed to windows or doors of old buildings are slightly thicker at the bottom than at the top.

Reason: Glass is a pseudosolid or supercooled liquid.

- 36. Assertion: The vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K.Reason: Vapour pressure of water is 1.013 bar at 373.15 K.
- **37. Assertion**: Frenkel defect is also called dislocation defect.

Reason: Frenkel defect is shown by ionic substances in which cation and anion are of almost similar sizes.

38. Assertion : Molecular mass of KCl calculated on the basis of colligative properties will be lower than the normal molecular mass.

Reason: Experimentally determined molar mass is always lower than the true value.

Match the Column

- 39. Match the column I with column II and mark the appropriate choice.
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	Column I		Column II
(A)	Ferromagnetic	(i)	$\uparrow \uparrow \downarrow \uparrow \uparrow$
(B)	Ferrimagnetic	(ii)	$\wedge \downarrow \wedge \downarrow \wedge \downarrow \wedge \downarrow$
(C)	Antiferromagnetic	(iii)	<u> </u>
(D)	Diamagnetic	(iv)	111111

- (a) $(A) \rightarrow (iii), (B) \rightarrow (i), (C) \rightarrow (ii), (D) \rightarrow (iv)$
- (b) (A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iii), (D) \rightarrow (iv)
- (c) $(A) \rightarrow (iv), (B) \rightarrow (i), (C) \rightarrow (iii), (D) \rightarrow (ii)$
- (d) (A) \rightarrow (i), (B) \rightarrow (iv), (C) \rightarrow (iii), (D) \rightarrow (ii)
- **40.** Match the column I with column II and mark the appropriate choice.

	Column I		Column II
(A)	$\Delta H_{\rm mix} = 0$, $\Delta V_{\rm mix} = 0$	(i)	Non-ideal solution
(B)	$\Delta H_{\rm mix} \neq 0$, $\Delta V_{\rm mix} \neq 0$	(ii)	Positive deviation
(C)	$\Delta H_{ m mix}$ < 0, $\Delta V_{ m mix}$ < 0	(iii)	Ideal solution
(D)	$\Delta H_{\text{mix}} > 0$, $\Delta V_{\text{mix}} > 0$		Negative deviation

- (a) $(A) \to (i), (B) \to (iii), (C) \to (ii), (D) \to (iv)$
- (b) (A) \to (iii), (B) \to (i), (C) \to (iv), (D) \to (ii)
- (c) $(A) \rightarrow (ii), (B) \rightarrow (iii), (C) \rightarrow (iv), (D) \rightarrow (i)$
- (d) (A) \rightarrow (iii), (B) \rightarrow (ii), (C) \rightarrow (i), (D) \rightarrow (iv)

Case Based MCQs

Case I: Read the passage given below and answer the following questions from 41 to 45.

In an ideal crystal, there must be regular repeating arrangement of the constituting particles and its entropy must be zero at absolute zero temperature. However, it is impossible to obtain an ideal crystal and it suffers from certain defects called imperfections. In pure crystal, these defects arises either due to disorder or dislocation of the constituting particles from their normal positions or due to the movement of the particles even at absolute zero temperature. Such defects increase with rise in temperature. In addition to this, certain defects arise due to the presence of some impurities. Such defects not only modify the existing properties of the crystalline solids but also impart certain new characteristics to them.

The following questions are multiple choice questions. Choose the most appropriate answer:

41. AgCl is crystallized from molten AgCl containing a little CdCl₂. The solid obtained will have

- (a) cationic vacancies equal to number of Cd²⁺ ions incorporated
- (b) cationic vacancies equal to double the number of Cd²⁺ ions
- anionic vacancies
- (d) neither cationic nor anionic vacancies.
- **42.** Lattice defect per 10¹⁵ NaCl is 1. What is the number of lattice defects in a mole of NaCl?
 - (a) 6.02×10^{23}
- (b) 6.02×10^8
- (c) 10^{14}
- (d) None of these
- 43. The ionic substances in which the cation and anion are of almost similar size shows
 - (a) non-stoichiometric defect
 - (b) Schottky defect
 - (c) Frenkel defect
 - (d) all of these.
- 44. If Al³⁺ ions replace Na⁺ ions at the edge centres of NaCl lattice, then the number of vacancies in 1 mole of NaCl will be
 - (a) 3.01×10^{23}
- (b) 6.02×10^{23}
- (c) 9.03×10^{23} (d) 12.04×10^{23}
- 45. Which of the following gives both Frenkel and Schottky defect?
 - (a) AgCl
- (b) CsCl (c) KCl
- (d) AgBr

Case II: Read the passage given below and answer the following questions from 46 to 50.

At 298 K, the vapour pressure of pure benzene, C_6H_6 is 0.256 bar and the vapour pressure of pure toluene C₆H₅CH₃ is 0.0925 bar. Two mixtures were prepared as follows:

- (I) $7.8 \text{ g of } C_6H_6 + 9.2 \text{ g of toluene}$
- (II) $3.9 \text{ g of } C_6H_6 + 13.8 \text{ g of toluene}$

The following questions are multiple choice questions. Choose the most appropriate answer:

- 46. The total vapour pressure (bar) of solution (I) is
 - (a) 0.128 (b) 0.174 (c) 0.198

- (d) 0.258
- 47. Which of the given solutions have higher vapour pressure?
 - (a) I

- (b) II
- (c) Both have equal vapour pressure
- (d) Cannot be predicted
- 48. Mole fraction of benzene in vapour phase in solution I is
 - (a) 0.128
- (b) 0.174 (c) 0.734
- (d) 0.266
- 49. Which of the following statements is/are correct?
 - (I) Mole fraction of toluene in vapour phase is more in solution I.

- (II) Mole fraction of toluene in vapour phase is less in solution I.
- (III) Mole fraction of benzene in vapour phase is less in solution I.
- (a) Only II
- (b) Only I
- (c) I and III
- (d) II and III
- 50. Solution I is an example of a/an
 - (a) ideal solution
 - (b) non-ideal solution with positive deviation
 - (c) non-ideal solution with negative deviation
 - (d) can't be predicted.

SOLUTIONS

- (d): Isotropical is not a crystal system type.
- 2. (b)
- 3. (c): No. of *X* atoms = $\frac{1}{8} \times 8 = 1$ No. of *Y* atoms = 1

No. of Z atoms =
$$12 \times \frac{1}{4} = 3$$

Hence, formula of the compound is XYZ_3 .

4. (c): Number of moles of glucose $(n_{C_6H_{12}O_6})$

$$=\frac{18}{180}=0.1\,\mathrm{mol}$$

Number of moles of water $(n_{H_2O}) = \frac{178.2}{18} = 9.9 \text{ mol}$

Mole fraction of water in solution $(x_{H_2O}) = \frac{9.9}{10} = 0.99$

Vapour pressure of water in aqueous solution,

 $p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^{\circ} \times x_{\text{H}_2\text{O}} = 760 \text{ torr} \times 0.99 = 752.4 \text{ torr}$

- 5. (d)
- 6. (c): Solubility of a gas ∞ mole fraction

$$n_{\text{N}_2} = \frac{5.5 \times 10^{-3}}{28} = 1.96 \times 10^{-4} \text{ at 1 atm}$$

Now, $p \propto$ mole fraction

so at 5 atm, the mole fraction will increase 5 times. Hence, mole fraction = $5 \times 1.96 \times 10^{-4} = 9.8 \times 10^{-4}$ $\approx 1.0 \times 10^{-3}$

- 7. (c)
- 8. (a): A mixture of chloroform (CHCl₃) and acetone (CH₃)₂CO shows negative deviations from Raoult's law due to formation of hydrogen bonds between the two molecules. Hence, a slight decrease in volume takes place.

9. (a):
$$2(r_{+} + r_{-}) = a$$

 $2(r_{Na^{+}} + r_{Cl^{-}}) = 564 \text{ pm}$
 $r_{Na^{+}} = \frac{564}{2} - 181 = 101 \text{ pm}$

10. (d): Hydrogen bonds are formed on mixing acetone and chloroform. The new interactions in the mixture are stronger than in the pure components. ΔV and ΔH are negative so, the solution will show a negative deviation.

11. (b): For bcc structure of ionic compounds like CsCl, Z = 1

$$d = \frac{Z \times M}{N_A \times a^3} \Rightarrow a^3 = \frac{Z \times M}{d \times N_A}$$
$$= \frac{1 \times 168.4}{3.988 \times 6.023 \times 10^{23}} = 7.010 \times 10^{-23} \text{ cm}^3$$

12. (d)

13. (b): FeO is mostly found with a composition of $Fe_{0.95}O$. In crystals of FeO, some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of the required number of Fe^{3+} ions.

14. (b)

15. (a): Paramagnetism occurs due to the presence of one or more unpaired electrons. They are weakly attracted by the magnetic field.

18. (d):
$$\Delta T_f = iK_f m$$

As m = 0.1 molal for all given solutions, thus, lower the value of i, lower will be the depression in freezing point (ΔT_f) and higher will be the freezing point of the solution.

For Al₂(SO₄)₃ ; i = 5For BaCl₂ ; i = 3For AlCl₃ ; i = 4For NH₄Cl ; i = 2

Thus, 0.1 molal NH₄Cl will have highest freezing point.

19. (d): Coordination number is defined as the number of nearest neighbours that an atom has in a unit cell. It depends upon structure.

For a simple cubic structure : coordination number = 6

20. (b): van't Hoff factor (*i*) expresses the extent of association or dissociation of solute in the solution.

21. (a):
$$\rho = \frac{Z \times M}{N_A \times a^3} \Rightarrow Z = \frac{\rho \times N_A \times a^3}{M}$$

$$= \frac{2.16 \times 6.023 \times 10^{23} \times (5.623 \times 10^{-8})^3}{M}$$

58.5

22. (a): Given: $K_f = 1.86 \text{ K kg mol}^{-1}$, w = 1.25 g, W = 50 g, $\Delta T_f = 0.3 ^{\circ}\text{C}$, M = ? As P undergoes association, $2P \Longrightarrow (P)_2$; n = 2 Using equation,

$$M = \frac{1000 \times K_f \times w}{W \times \Delta T_f} \implies M = \frac{1000 \times 1.86 \times 1.25}{50 \times 0.3} = 155$$

Now,
$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = \frac{94}{155} = 0.606$$

Then, the degree of association of P is

$$\alpha = \frac{1 - i}{1 - \frac{1}{n}} \implies \alpha = \frac{1 - 0.606}{1 - \frac{1}{2}} = 0.788 = 78.8\% \approx 80\%$$

23. (b): Density =
$$\frac{Z \times M}{N_A \times a^3}$$

= $\frac{4 \times 58.5}{6.023 \times 10^{23} \times (5.64 \times 10^{-8})^3} = 2.16 \text{ g/cm}^3$

24. (c): The given figure is showing positive deviation from Raoult's law.

$$P_A > P_A^{\circ} X_A$$

Thus A - B attractive force should be weaker than A - A and B - B attractive forces.

25. (a): p-type semiconductors are made by adding impurity of previous group elements. For making p-type semiconductor of Ge (14th group), it should be doped with trivalent impurity.

26. (c)

27. (a): In Schottky defect equal number of cations and anions are missing from the lattice, so that equal number of cation and anion vacancies are produced.

28. (b): Since number of particles of AlCl₃ in solution is more than that of CaCl₂, ΔT_b of AlCl₃ is more. Hence, boiling point of AlCl₃ solution is higher.

29. (c): For octahedral arrangement radius ratio limits is 0.414 to 0.732.

30. (c): Molality,
$$m = \frac{M}{1000d - MM_2} \times 1000$$

where, M = molarity, d = density, $M_2 = \text{molecular mass}$

$$m = \frac{2.05}{1000 \times 1.02 - 2.05 \times 60} = \frac{2.05}{897}$$
$$= 2.28 \times 10^{-3} \text{ mol g}^{-1} = 2.28 \text{ mol kg}^{-1}$$

31. (d): Number of atoms of element A per unit cell = 8

(at corners)
$$\times \frac{1}{8} = 1$$
]

No. of atoms of B in one unit cell = 1 (present in the body centre of the cube).

The number of atoms of elements *A* and *B* per unit cell is one each. Hence, the formula is AB.

32. (d):
$$P_{\text{Total}} = p_A x_A + p_B x_B$$

= $100 \times \frac{2}{5} + 80 \times \frac{3}{5} = 88 \text{ torr}$

33. (b): As equal number of Na⁺ and Cl⁻ ions are missing from the crystal, hence it is showing Schottky defect.

34. (a):
$$\Delta T_f = 1.86 \times \left(\frac{342}{342}\right) = 1.86 \,^{\circ}\text{C}$$

:.
$$T_f = -1.86 \, ^{\circ}\text{C}$$

35. (a)

36. (b): This is due to relative lowering of vapour pressure on adding solute.

37. (c): Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions.

38. (c): The molecular mass of KCl is lower than the normal molecular mass because they undergo dissociation when dissolved in the solvent.

41. (a): In the crystallisation, some Ag⁺ ions will get replaced by Cd²⁺ ions and each Cd²⁺ ion replaces two Ag⁺ions so as to maintain electrical neutrality. Thus, the cation vacancies will be the same as the number of Cd²⁺ ions incorporated.

42. (b): Number of defects per mole of NaCl

$$=\frac{1\times6.02\times10^{23}}{10^{15}}=6.02\times10^{8}$$

43 (b): Schottky defect is shown by highly ionic compounds, e.g., NaCl, KCl, KBr, AgBr, CsCl, etc.

44 (a): There are 12 edge centres.

Contribution of Na⁺ ions at edge centres = $12 \times \frac{1}{4} = 3$ Besides, there is one Na⁺ ion at body centre.

Thus, there are four Na⁺ ions per unit cell.

$$\frac{3}{4}$$
 are replaced by Al³⁺ ions.

Total Na⁺ ions in 1 mole of NaCl = 6.023×10^{23} Na^{+} ion replaced by $\text{Al}^{3+} = 3/4 \times 6.023 \times 10^{23}$

1 Al³⁺ replaces 3 Na⁺ ions thereby creating 2 vacancies.

$$\therefore \text{ No. of vacancies created} = \frac{2}{3} \times \left(\frac{3}{4} \times 6.023 \times 10^{23} \right)$$
$$= 3.01 \times 10^{23}$$

45. (d)

46. (b): Moles of
$$C_6H_6 = \frac{7.8}{78} = 0.1$$

Moles of
$$C_6H_5CH_3 = \frac{9.2}{92} = 0.1$$

Mole fraction of
$$C_6H_6 = \frac{0.1}{0.1 + 0.1} = 0.5$$

Mole fraction of $C_6H_5CH_3 = 0.5$

Vapour pressure of toluene = Vapour pressure of pure toluene × mole fraction of toluene

$$= 0.0925 \times 0.5 = 0.04625$$

Vapour pressure of benzene = $0.256 \times 0.5 = 0.128$ Total vapour pressure of solution = 0.04625 + 0.128= 0.17425

47. (a): Moles of benzene in solution-II = $\frac{3.9}{78}$ = 0.05

Moles of toluene in solution-II = $\frac{13.8}{92}$ = 0.15

Mole fraction of C_6H_6 in solution (II) = $\frac{0.05}{0.05 + 0.15} = 0.25$

Mole fraction of
$$C_6H_5CH_3 = \frac{0.15}{0.05 + 0.15} = 0.75$$

Vapour pressure of solution

$$= 0.256 \times 0.25 + 0.0925 \times 0.75$$
$$= 0.064 + 0.06937 = 0.13375$$

48. (c): Mole fraction of benzene in vapour phase

$$y_{\text{benzene}} = \frac{p_{\text{benzene}}}{P_{\text{total}}} = \frac{0.128}{0.17425} = 0.734$$

49. (a): Mole fraction of toluene in vapour phase in

solution-I =
$$\frac{0.04625}{0.17425}$$
 = 0.2654

Mole fraction of toluene in vapour phase in solution-II

$$=\frac{0.06937}{0.13375}=0.519$$

Mole fraction of toluene in vapour phase in solution-II is greater than in solution-I.

Hence, statement II is correct.

Mole fraction of benzene in vapour phase in solution – I = 0.734

Mole fraction of benzene in vapour phase in solution-II = $\frac{0.064}{0.13375}$ = 0.478

Thus, mole fraction of benzene in vapour phase is less in solution-II.

50. (a): Benzene and toluene form an ideal solution.



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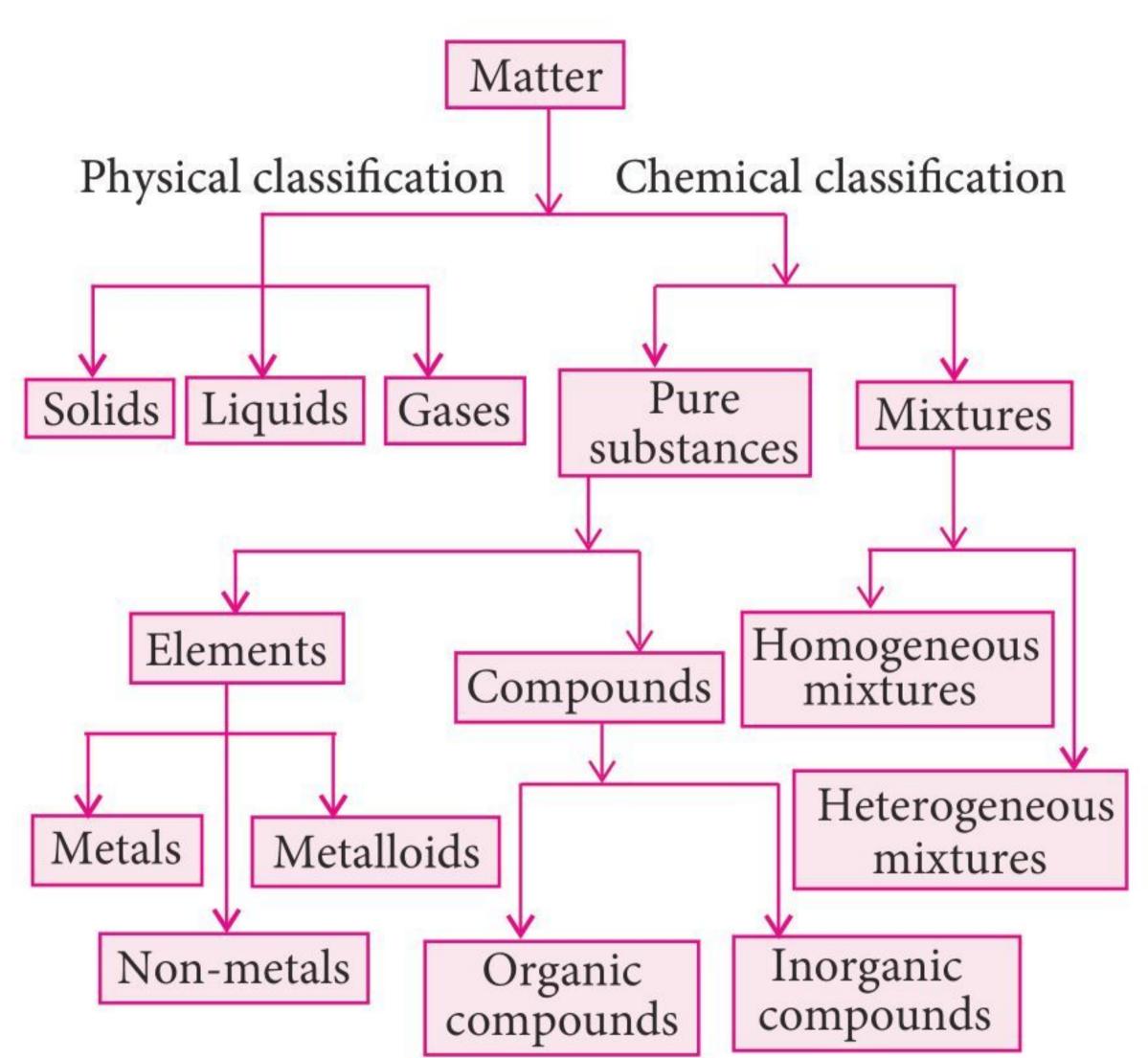
Some Basic Concepts of Chemistry | Structure of Atom

Some Basic Concepts of Chemistry

MATTER

• Anything which occupies space and has mass is called matter.

Classification of Matter



Dalton's Atomic Theory

The main postulates of Dalton's atomic theory are the following:

- Elements consist of small, indivisible, indestructible particles called atoms.
- Atoms of an element are identical to each other.
- They have the same mass and size.

- Chemical reactions involve reorganisation of atoms.
- Atoms cannot be created, destroyed or transformed into atoms of other element.
- Atoms of different elements differ in properties and have different masses and sizes.
- The relative numbers and kind of atoms are always the same in a given compound.

Atoms and Molecules

- An atom is the smallest particle of an element which can take part in a chemical reaction. It may or may not be capable of independent existence.
- A molecule is the smallest particle of an element or a compound which is capable of independent existence.
- **Elements** Pure substance that contains only one kind of atoms \rightarrow C, H, O, etc.
- **Compounds** Pure substance which is formed by combining two or more elements in a definite ratio \rightarrow CO₂, H₂O
- Mixtures

 → Made by mixing two or more substances in any ratio.

 → Air, tap water

S.I. Units (International System of Units)

• The International System of Units (SI, in French Systeme Internationale) or metric system, is a decimal system of unit for measurement of mass, length, time (fundamental units) and other physical quantities (desired units).

Precision and Accuracy

Every experimental measurement has some amount of uncertainty associated with it. However, one would always like the results to be precise and accurate.

- Precision: It refers to the closeness of various measurements for the same quantity.
- **Accuracy:** It is the agreement of a particular value to the true value of the result.

Significant Figures

- The total number of meaningful digits in a number which are known with certainty is called the number of significant figures (S.F.). It equals the number of digits written including the last one, even though its value is uncertain. The following rules should be followed in counting of S.F. in a given measured quantity.
 - All non-zero digits are significant.
 - The zeros to the right of the decimal point are significant.
 - Zeros between two non-zero digits are significant.
 - The zeroes to the left of first non-zero digit in a number are not significant.
 - The above rules propose that the numbers are expressed in scientific notation. In this term, every number is written as $N \times 10^n$, where N = a number with a single non-zero

digit to the left of the decimal point, n = aninteger We can write 20,000 in scientific notation as 2×10^4 2.0×10^4 2.00×10^{4}

1 S.F. 2 S.F. 3 S.F having

- Zero at the end of a number are significant provided that they are on the right side of the decimal point.

S.F. in numerical calculations

To express the result of an experiment, we have to often add, subtract, multiply or divide the numbers obtained in different measurements.

Rule I: S.F. rule in multiplication/division

The result of multiplication and/or division may carry no more S.F. than the least precisely known quantity in the calculation.

Rule II: S.F. rule in addition/subtraction

The result of addition and/or subtraction must be expressed with the same number of decimal places as the term carrying the smallest number of decimal places.

Rule III: S.F. rule for each exact number

Exact numbers can be considered to have an unlimited number of S.F.

"Rounding off" the numerical results

To three S.F., we should express 15.453 as 15.5 and 14755 as 1.48×10^4 . It is called "Rounding off" the result.

- If the first digit removed is less than 5, round down by dropping it and all following digits. Thus, 5.663507 becomes 5.66 when rounded off to three S.F. because first of the dropped digits (3) is less than 5.
- If the first digit removed is 6 or greater than 6 round off by adding 1 to the digit on the left.
- If the digit removed is 5 and there is no digit after, then add one to the preceeding digit if it is odd, otherwise write as such if it is even.

LAWS OF CHEMICAL COMBINATION

Law of Conservation of Mass

It states that during any physical or chemical change, total mass of products is equal to the total mass of reactants.

Law of Constant Composition or Definite **Proportions**

It states that a given compound always contains exactly the same definite proportion of elements by weight.

Law of Multiple Proportions

It states that when two or more elements combine to form two or more compounds, the different weights of one of the elements which combine with the fixed weight of the other element bear a simple whole number ratio to one another.

Gay Lussac's Law of Gaseous Volumes

It states that under similar conditions of temperature and pressure, whenever gases react together, the volumes of the reacting gases as well as products bear a simple whole number ratio.

Avogadro's law/hypothesis: "Equal volumes of gases under similar conditions of temperature and pressure should contain equal number of molecules".

ATOMIC AND MOLECULAR MASSES

Atomic Mass

It is the average relative mass of atom of element as compared with $\frac{1}{12}$ times the mass of an atom of carbon-12 isotope.

Atomic mass =
$$\frac{\text{Average mass of an atom}}{1/12 \times \text{Mass of an atom of}}$$

Calculation of Atomic Weight (Dulong and Petit's law for solids)

• Atomic wt. \times specific heat = 6.4 approx

$$\therefore \text{ Approx. atomic weight} = \frac{6.4}{\text{Sp. heat}}$$

$$Valency = \frac{At. wt.}{Eq. wt.}$$

Exact atomic weight = Eq. wt. \times valency

Molecular Mass

Molecular mass of a molecule of an element or a compound may be defined as a number which indicates how many times heavier is a molecule of that element

or compound as compared with $\frac{1}{12}$ of the mass of an atom of carbon-12. Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together.

Molecular mass is also expressed in a.m.u.

Molecular mass =
$$\frac{\text{Mass of one molecule of the substance}}{1/12 \times \text{Mass of one atom of C-12}}$$

Actual mass of one molecule

= Mol. mass (in amu)
$$\times 1.66 \times 10^{-24}$$
 g

Calculation of Molecular Weight

- Molecular mass = $2 \times \text{Vapour density}$
- Molecular mass = Mass of 22.4 L of vapour at STP
- Rates of diffusion, $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

Gram Equivalent Mass

The quantity of a substance whose mass (in grams) is numerically equal to its equivalent mass is called its one gram equivalent or gram equivalent mass (GEM).

Thus, Number of gram equivalent

Acidity

Calculation of equivalent weight

• Eq. wt. of an acid =
$$\frac{\text{Mol. wt. of the acid}}{\text{Basicity}}$$

Eq. wt. of a base = $\frac{\text{Mol. wt. of the base}}{\text{Mol. wt. of the base}}$

$$Eq. wt. of a salt = \frac{Mol. wt. of the salt}{Total positive valency of the}$$

$$metal atoms$$

• Eq. wt. of oxidizing/reducing agent

Mol. wt. of the substance

No. of electrons gained/lost by one molecule

Mole Concept

- One mole is the amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g of 12 C isotope ($\approx 6.023 \times 10^{23}$ atoms/mol of C^{12}).
- No. of moles of a substance (n)

- 1 Mole of atoms = Gram atomic mass (or 1 g atom) = 6.022×10^{23} atoms
- 1 Mole of molecules = Gram molecular mass (or 1 g molecule) = 6.022×10^{23} molecules = 22.4 L at STP

Determination of Chemical Formula

- Empirical formula gives the simplest whole number ratio of the atoms of various atoms present in a compound.
- Molecular formula gives the actual number of atoms of various elements present in one molecule of the compound.
- Molecular formula = $n \times$ empirical formula, where n = 1, 2, 3, ...

Percentage Composition

- Mass percentage of an element in a compound
 - $= \frac{\text{Mass of that element in the compound}}{\text{Molecular mass of the compound}} \times 100$

Percentage Yield

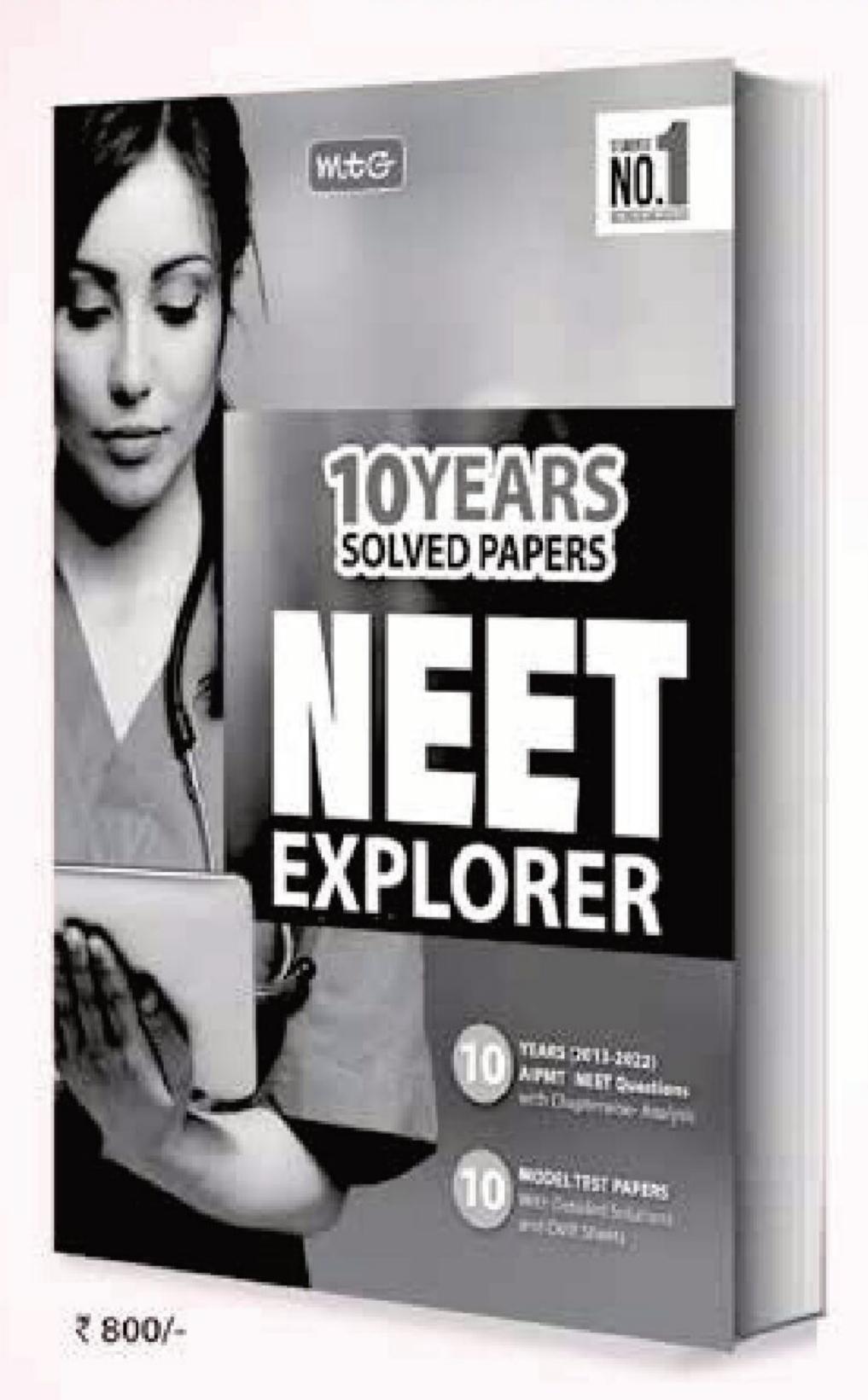
• Percentage yield = $\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$

STOICHIOMETRY

One of the most important aspects of a chemical equation is that when it is written in the balanced form, it gives quantitative relationship between the various reactants and products in terms of moles, molecules, masses and volumes. This is called stoichiometry (Greek word meaning 'to measure an element').



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Mass Percent

Mass percent =
$$\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

Mole Fraction

Mole fraction of a substance A' in a solution No. of moles of A

Total number of moles of solution

Molarity

 $Molarity = \frac{Number of moles of solute}{Volume of solution in litres}$

Molality

$$Molality = \frac{Number of moles of solute}{Mass of solvent in kg}$$

Structure of Atoms

SUB-ATOMIC PARTICLES

- Dalton's atomic theory proposed that matter is composed of small, indivisible particles called atoms.
- However, atoms are further composed of fundamental particles *i.e.*, electrons, protons and neutrons.
- Electrons and protons were discovered by passing electric discharge through discharge tube at very low pressure and at very high voltages.
 - Invisible rays travelling from cathode to anode producing fluorescence indicated the presence of electrons in atoms.
 - Anode rays moving from anode to cathode suggested the presence of positively charged protons.
 - Neutrons were discovered by bombarding a thin sheet of beryllium element with α -particles.
- **Isotopes** are atoms of same element having same atomic number but different mass numbers.

 35Cl and 37Cl are examples of isotopes.
- **Isobars** are atoms of different elements with same mass number but different atomic numbers.

 40 K and 40 Ca are examples of isobars.
- **Isotones** are atoms of different elements having same number of neutrons in the nucleus.

 15 N and 16 O are examples of isotones.

ATOMIC MODELS

Thomson's Model of Atom

• According to Thomson's atomic model, an atom consists of a uniform sphere in which positive

- charge is uniformly distributed. The electrons are embedded into it in such a way so as to give the most stable electrostatic arrangement.
- Although the model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments.

Rutherford's Nuclear Model of Atom

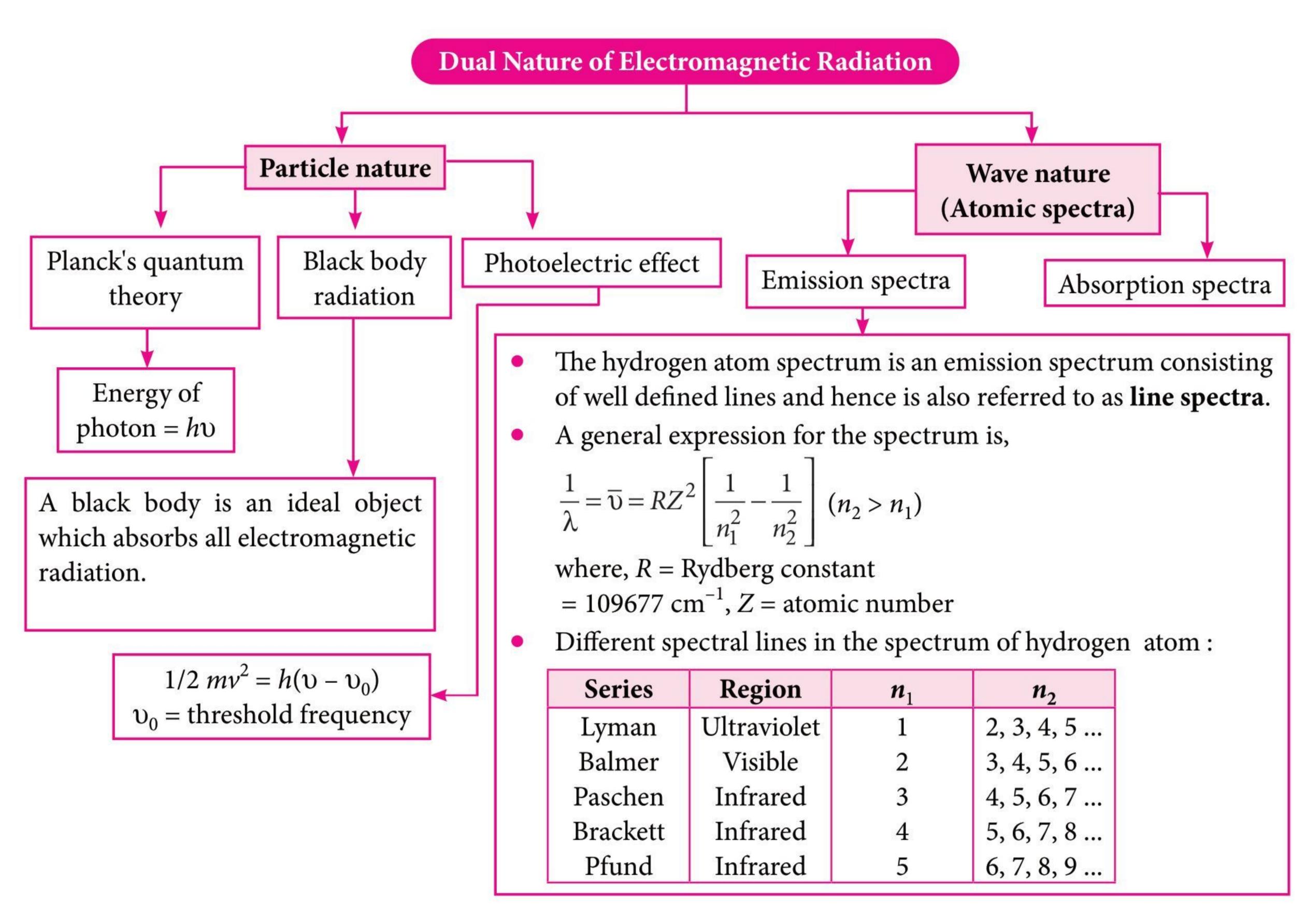
Rutherford discovered the nucleus by bombarding a thin gold foil by fast moving α -particles.

Postulates

- Atom is spherical and consists of two parts, nucleus and extranuclear part.
- Nucleus is very small in size. It is a positively charged, highly dense central core in which entire mass of the atom is concentrated.
- Extranuclear part is an empty space around the nucleus where electrons are revolving in a circular orbit with very high speed. This nuclear model is comparable to our solar system in which planets are revolving around the sun. Electrons and the nucleus are held together by electrostatic forces of attraction.

NATURE OF ELECTROMAGNETIC RADIATION

- Waves having both electric and magnetic fields associated with them are referred to as electromagnetic radiations, and the arrangement of different types of electromagnetic radiations in the order of increasing wavelengths or decreasing frequencies is known as **electromagnetic spectrum**.
- Electromagnetic waves are considered to have dual nature *i.e.*, particle nature and wave nature.



DUAL BEHAVIOUR OF MATTER

- In 1924, de Broglie proposed that matter, like radiation, behaves both as a material and as a wave. This proposal gave birth to wave mechanical theory which states that electrons, protons and even atoms when in motion possess wave properties.
- The de Broglie wavelength of a particle is given by $\lambda = \frac{h}{mv} = \frac{h}{p}$

where, h = Planck's constant, m = mass of particle, v = velocity, p = momentum

• Let kinetic energy of the particle of mass 'm' be E.

$$E = \frac{1}{2}mv^2; \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

Bohr's Model of an Atom

- Bohr's model of an atom is based upon Planck's quantum theory. The main postulates of this model are as follows:
 - Electrons revolve only in certain definite orbits around the nucleus. These are called stationary states because they have fixed energies. These

- are called 1st, 2nd, 3rd, 4th or K, L, M, N, etc.
- Electrons revolve only in those orbits for which angular momentum is an integral multiple of

$$h/2\pi$$
, i.e., $mvr = n\frac{h}{2\pi}$; $n = 1, 2, 3....$

 When electron jumps from one level to another, energy is either emitted or absorbed.

The energy difference between two states is given by : $\Delta E = E_2 - E_1$.

As the distance of the orbits increases from the nucleus, the energy gap goes on decreasing, *i.e.*, $E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > \dots$

- Quantization of electronic energy and momenta: The energy as well as angular momenta of the electrons in an atom are quantized.
- Energy of the electron in the n^{th} orbit :
 - For hydrogen-like particles (containing one electron only like He⁺, Li²⁺, etc.), is given by

$$E_n = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$$

Where, m = mass of electron, e = charge on the electron, Z = atomic number of the element,

h = Planck's constant.

For H-atom, Z = 1, the energy of electron in the n^{th} orbit is :

$$E_n = -\frac{21.78 \times 10^{-19}}{n^2} \text{ J atom}^{-1}$$

$$= -\frac{13.6}{n^2} \text{ eV atom}^{-1} (1 \text{ eV} = 1.602 \times 10^{-19} \text{ J})$$

$$= -\frac{1312}{n^2} \text{ kJ mol}^{-1} = -\frac{313.6}{n^2} \text{ kcal mol}^{-1}$$

- Radii of the orbits: For H-like atom, the radius of the n^{th} orbit is given by $r_n = r_0 \frac{n^2}{Z}$ where, $r_0 = 0.529 \text{ Å} = 52.9 \text{ pm}$ is the radius of the first orbit of hydrogen atom (called Bohr radius). For H-atom, the radius of the n^{th} orbit will be given by $r_n = r_0 n^2$.
- **Velocity of electron in** n^{th} **orbit :** For H-like particles, it is given by $v_n = v_0 \times \frac{Z}{n}$ where $v_0 = 2.188 \times 10^8 \text{ cm s}^{-1}$ is the velocity of the electron in the first orbit of hydrogen atom. It is nearly $1/137^{\text{th}}$ velocity of light.

Heisenberg's Uncertainty Principle

• It states that "It is impossible to measure simultaneously the position and momentum of a microscopic particle with absolute accuracy. If one of them is measured with greater accuracy, the other becomes less accurate. The product of their uncertainties is always equal to or greater than $\frac{h}{4\pi}$. Mathematically, $\Delta x \times \Delta p \ge \frac{h}{4\pi}$ where, $\Delta x =$ uncertainty in position, $\Delta p =$ uncertainty in momentum.

• Significance of Heisenberg's uncertainty principle:

- It overruled the existence of definite paths or trajectories of electrons and other similar particles.
- It holds for microscopic objects only and is negligible for macroscopic objects.

QUANTUM MECHANICAL MODEL OF ATOM

- Schrodinger wave equation for hydrogen atom is given by $\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E V) \Psi = 0$
- ψ has no physical significance but ψ^2 describes the probability of finding an electron within a small space.
- An atomic orbital may be defined as three dimensional space around the nucleus where the probability of finding an electron is maximum.
- The probability of locating the electron at different distances from the nucleus can be represented graphically by plotting probability (ψ^2) against the distance (r) from the nucleus of the atom. Such a plot of probability versus distance is known as **probability distribution curve**.
- The radial probability distribution of the electron is obtained by plotting the function $4\pi r^2 \psi^2$ against the distance r from the nucleus.
- In the plots of radial probability versus distance from the nucleus, number of peaks, *i.e.*, regions of maximum probability = n 1 (number of radial nodes = n l 1).
- A nodal plane is the plane on which the probability of finding the electron is zero.
- The distance of maximum probability for 1*s* electron of hydrogen atom is 0.53 Å and it is equal to Bohr's radius for the first orbit.

QUANTUM NUMBERS

	Principal quantum number (n)	Azimuthal or angular quantum number (<i>l</i>)	Magnetic quantum number (<i>m</i>)	Spin quantum number (s)
Used to	specify the position and energy of electron.		determine the preferred orientation of orbitals in space.	Account for the spin of electrons.
Values	$n = 1, 2, 3,, \infty$	l = 0, 1, 2,, (n - 1)	-l 0 +l	+1/2 or -1/2

Used for Calculating	Maximum number of electrons = $2n^2$ $E_n = \frac{-13.6 Z^2}{n^2}$	Orbital angular momentum $\frac{h}{2\pi} \sqrt{l(l+1)}$ s	$d \Longrightarrow m = \pm 2, \pm 1, 0$	Spin angular momentum $= \frac{h}{2\pi} \sqrt{s(s+1)}$ $s \Rightarrow \text{maximum 2 electrons}$ $p \Rightarrow \text{maximum 6 electrons}$ $d \Rightarrow \text{maximum 10 electrons}$ $f \Rightarrow \text{maximum 14 electrons}$
			(7 values)	
Examples	1, 2, 3, 4, 5, 6, 7 KLMNOPQ	0, 1, 2, 3 s p d f		

SHAPES OF ATOMIC ORBITALS

Shape of an orbital is given by total probability density, ψ^2 including both radial part as well as angular part.

Shape of s-orbital

Shape of *s*-orbital must be spherical since probability of finding electron is equal in all directions at a distance from nucleus.

Shape of *p*-orbital

The probability of finding *p*-electron is maximum in two dumb-bell type lobes on the two opposite sides of nucleus. Thus, p-orbital has dumb-bell shape. In the three p-orbitals, p_x , p_y and p_z the probability lies maximum along x-axis, y-axis and z-axis respectively.

Shape of *d*-orbital

Depending on the probability, d-orbitals have cloverleaf shape. There are five d-orbitals, d_{xy} , d_{yz} , d_{xz} , d_{xz-y^2} and d_{z^2} . d_{z^2} has exceptionally doughnut shape. Each *d*-orbital has two nodal-planes.

- Number of radial nodes = (n l 1)
- Number of angular nodes = l
- Total number of nodes = (n 1)
- Number of nodal planes = l

Electronic Configuration

- Electrons are distributed in different orbitals in an atom and this arrangement is referred to as electronic configuration.
- The filling up of electrons in different orbitals is based on the following rules:
 - Aufbau's principle: Electrons are progressively added to the different orbitals in their increasing order of energy.

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p <

Pauli's exclusion principle: No two electrons

in an atom can have the same set of all the four quantum numbers.

Hund's rule of maximum multiplicity: Electron pairing in an orbital of same energy takes place only when each orbital is singly filled.

Greater stability of exactly half-filled and completely-filled configurations

Elements with atomic number 24(Cr) and 42(Mo) have $ns^{1}(n-1)d^{5}$ configuration and not $ns^{2}(n-1)d^{4}$, due to extra stability of half-filled orbitals.

$$\begin{array}{c|c}
4s & 3d \\
\hline
 & \uparrow & \uparrow & \uparrow & \uparrow \\
\hline
 & \uparrow & \uparrow & \uparrow & \uparrow
\end{array}$$

Elements with atomic number ²⁹Cu, ⁴⁷Ag and ⁷⁹Au have $ns^{1}(n-1)d^{10}$ configuration and not $ns^{2}(n-1)d^{9}$ due to extra stability of fully filled orbitals.

- This is because of
 - Symmetry: The half-filled and completely filled configurations are more symmetrical and symmetry leads to greater stability.
 - Exchange energy: The electrons present in the different orbitals of the same subshell can exchange their positions. Each such exchange results in release of energy (called exchange energy), which leads to a greater stability.

MONTHLY TEST DRIVE CLASS XII

- (c) (a) (a) (b) (b) (a) (d) **10.** (c)
- **11**. (b) **12.** (a) **13.** (a) **14**. (b) **15**. (b)
- **16.** (c) **18.** (a) **17**. (a) **20**. (b,d)
- **21**. (a,c,d) **22**. (a,b,c) **23**. (a,c) **24**. (3) **25**. (2)



MCQs TYPE QUESTIONS

- 1. Which element has a hydrogen like spectrum whose lines have wavelength one fourth of atomic hydrogen?

- (a) He^+ (b) Li^{2+} (c) Be^{3+} (d) B^{4+}
- 2. If the threshold frequency of a metal for photoelectric effect is u_0 , then which of the following will not happen?
 - (a) If frequency of the incident radiation is u_0 , then kinetic energy of the electrons ejected is zero
 - (b) If frequency of incident radiation is u, then kinetic energy of the electrons ejected will be $hu-hu_0$.
 - (c) If frequency is kept same at u, but intensity is increased, then number of electrons ejected will increase.
 - (d) If frequency of incident radiation is further increased, then number of electrons ejected will increase.
- 3. Three isotopes of an element have mass numbers, M, (M + 1) and (M + 2). If the mean mass number is (M + 0.5) then which of the following ratio may be accepted for M, (M + 1), (M + 2) in that order (a) 1:1:1 (b) 4:1:1(c) 3:2:1 (d) 2:1:2
- 4. Consider the following sets of quantum numbers:

	n	1	m	S
(i)	3	0	0	+ 1/2
(ii)	2	2	1	+ 1/2
(iii)	4	3	-2	- 1/2
(iv)	1	0	-1	- 1/2
(v)	3	2	3	+ 1/2

Which of the following sets of quantum number is not possible?

- (a) (i), (ii), (iii) and (iv) (b) (ii), (iv) and (v)
- (c) (i) and (iii) (d) (ii), (iii) and (iv)
- 5. If $a = \frac{h}{4\pi^2 me^2}$, then the correct expression for calculation of the circumference of the first orbit of hydrogen atom should be
 - (a) $\sqrt{4h^2\pi a}$
- (b) $2\pi r$

- (c) $\sqrt{4\pi ha}$
- (d) both (a) and (c) are correct
- With increasing principal quantum number, the energy difference between adjacent energy levels in H atom
 - (a) decreases
- (b) increases
- remains constant
- (d) decreases for low value of Z and increases for higher value of Z.
- **Assertion:** 1 mole $O_3 = N$ molecules of $O_3 = 3N$ atoms of O = 48 g.

Reason: A mole is the amount of matter that contains as many as objects as the number of atoms exactly in 12 g C^{12} .

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- **Assertion**: The value of *n* for a line in Balmer series of hydrogen spectrum having the highest wavelength is 4 and 6.

Reason: For Balmer series of hydrogen spectrum, the value $n_1 = 2$ and $n_2 = 3, 4, 5$.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- The frequency of radiation emitted when the electron falls from n = 4 to n = 1 in a hydrogen atom will be (Given ionization energy of H = 2.18×10^{-18} J atom⁻¹ and $h = 6.625 \times 10^{-34} \text{ J s}$

- (a) $1.54 \times 10^{15} \text{ s}^{-1}$ (b) $1.03 \times 10^{15} \text{ s}^{-1}$ (c) $3.08 \times 10^{15} \text{ s}^{-1}$ (d) $2.00 \times 10^{15} \text{ s}^{-1}$

- 10. 12 g of Mg (atomic mass = 24) on reacting completelywith acid gives hydrogen gas, the volume of which at STP would be
 - (a) 22.4 L (b) 11.2 L (c) 44.8 L (d) 6.1 L

- 11. The de-Broglie wavelength of a particle with mass 1 g and velocity 100 m/s is
 - (a) 6.6×10^{-33} m (b) 6.6×10^{-34} m
- - (c) 6.6×10^{-35} m (d) 6.6×10^{-35} m
- 12. The maximum number of electrons in a subshell is given by the expression

 - (a) 4l-2 (b) 4l+2 (c) 2l+1 (d) $4n^2$

- 13. Match the mass of elements given in column I with the number of moles given in column II and select the correct option.

Column I		Column II	
(A)	28 g of He	(p)	2 moles
(B)	46 g Na	(q)	7 moles
(C)	60 g of Ca	(r)	1 mol
(D)	27 g of Al	(s)	1.5 moles

- (a) A (s), B (r), C (q), D (p)
- (b) A (p), B (r), C (q), D (s)
- (c) A (r), B (q), C (p), D (s)
- (d) A (q), B (p), C (s), D (r)
- 14. The correct order of increasing energy of atomic orbitals is

 - (a) 5p < 4f < 6s < 5d (b) 5p < 6s < 4f < 5d

 - (c) 4f < 5p < 5d < 6s (d) 5p < 5d < 4f < 6s
- 15. n g of substance X react with m g of substance Y to form p g of substance R and q g of substance S. This reaction can represented as, X + Y = R + S. The relation which can be established in the amount of the reactants and the products will be

 - (a) n m = p q (b) n + m = p + q
 - (c) n=m (d) p=q
- **16.** 1.0 g of an oxide of *A* contained 0.5 g of *A*. 4.0 g of another oxide of A contained 1.6 g of A. The data indicate the law of
 - (a) reciprocal proportions
 - (b) constant proportions
 - (c) conservation of energys
 - (d) multiple proportions.
- 17. Subsidiary quantum number specifies
 - (a) size of orbital
 - (b) shape of orbital

- (c) orientations of orbital
- (d) nuclear stability.
- 18. Which of the following relates to photons both as wave motion and as stream of particles?
 - (a) Interference (b) $E = mc^2$
- - (c) Diffraction (d) E = hv
- 19. Which of the following is not correct for electronic distribution in the ground state?
 - (a) $Co = [Ar] \uparrow \downarrow$
- (b) Ni = [Ar] $\uparrow \downarrow$
- (c) $Cu = [Ar] \uparrow \downarrow$ (d) $Zn = [Ar] \uparrow \downarrow$
- 20. The radius of which of the following orbits is same as that of the first Bohr's orbit of hydrogen atom?
 - (a) He^+ (n=2) (b) Li^{2+} (n=2)
- - (c) Li^{2+} (n=3)
- (d) Be³⁺ (n = 2)

NUMERICAL VALUE TYPE QUESTIONS

- 21. Calculate the mass of oxygen required (in g) to burn 14 g of C_2H_4 completely.
- 22. The momentum of radiations of wavelength 0.33 nm is $x \times 10^{-24} \text{ kg ms}^{-1}$. Then the value of x is _____.
- 23. What is the volume (in mL) of N/4 NaOH required to neutralize 100 mL of N/2 HCl?
- 24. What is the uncertainty in the position of a particle (in m) when the uncertainty in the momentum is infinity?
- 25. Calculate the energy required (in kJ mol⁻¹) to shift all the electrons from the 1st Bohr's orbit to the fifth Bohr's orbit in one mole of hydrogen.

SOLUTIONS

1. (a): $\frac{1}{\lambda_{H}} = R \times 1^{2} \left(\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}} \right)$

$$\frac{1}{\lambda_X} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad ...(ii)$$

Dividing equation (i) by equation (ii) we get

$$=\frac{\lambda_X}{\lambda_H} = \frac{1}{Z^2}; \frac{1}{4} = \frac{1}{Z^2}; Z = 2 \text{ (He}^+)$$

- (d)
- **(b)**: Let M: (M+1): (M+2) = 4:1:1

$$\frac{M \times x + (M+1)y + (M+2)z}{x + y + z} = M + 0.5$$

0.5x + 0.5y + 0.5z = y + 2z

0.5x = 0.5y + 1.5z $\therefore x = y + 3z$

therefore, the ratio of M: (M + 1): (M + 2) = 4:1:1

5. (d): Circumference =
$$2\pi r$$

$$2 \times \pi \times \frac{n^2 h^2}{4\pi^2 m Z e^2}$$
, $n = 1$, $Z = 1$ and $\frac{h}{4\pi^2 m e^2} = a$

Thus,
$$2 \times \pi \times h \times a$$
 or $\sqrt{4}\pi ha$ or $\sqrt{4}h^2\pi a$

9. (c):
$$E = hv$$
 or $v = E/h$

For H atom
$$E = \frac{-21.76 \times 10^{-19}}{n^2}$$
 J atom⁻¹

$$\Delta E = -21.76 \times 10^{-19} \left(\frac{1}{4^2} - \frac{1}{1^2} \right) = 20.40 \times 10^{-19} \text{ J atom}^{-1}$$

$$v = \frac{20.40 \times 10^{-19} \text{ J/atom}}{6.626 \times 10^{-34} \text{ Js}} = 3.08 \times 10^{15} \text{ s}^{-1}$$

10. (b):
$$Mg + 2HX \longrightarrow MgX_2 + H_2$$

$$\begin{array}{ccc}
1 & mol & Acid & 1 & mol \\
(24 & g) & & (22.4 & I)
\end{array}$$

Thus, 12 g Mg gives 11.2 L of hydrogen gas.

11. (a):
$$\lambda = \frac{h}{}$$

$$m = 1$$
 $g = 10^{-3}$ kg, $v = 100$ m/s, $h = 6.626 \times 10^{-34}$ J s⁻¹ 6.626×10^{-3} kg m²s⁻¹ Hence,

$$\lambda = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{s}^{-1}}{10^{-3} \text{ kg} \times 100 \text{ m s}^{-1}} = 6.6 \times 10^{-33} \text{ m}$$

14. (b): For
$$4f(n+l) = 4+3=7$$

For
$$5p(n+l) = 5+1=6$$

For
$$6s(n+1) = 6+0=6$$

For
$$5d(n+1) = 5 + 2 = 7$$

Thus, order of increasing energy is:

15. (b):
$$X + Y \rightleftharpoons R + S$$
 $n g m g p g q g$

$$n+m=p+q$$

by law of conservation of mass.

16. (d)

17. (b): Subsidiary quantum number (*l*) describes the shape of orbital.

20. (d): Applying,
$$r_n = \frac{r_0 \times n^2}{Z}$$
 where r_0 is the radius of

1st Bohr orbit or ground state of H-atom

As given,
$$\frac{r_0 \times n^2}{Z} = r_0$$

i.e.,
$$n^2 = Z$$
 which is possible only for Be³⁺
For Be³⁺, $n = 2$, $Z = 4$ \therefore $n^2 = Z = 4$

21. (48):
$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

Moles of C₂H, to be burnt =
$$\frac{14}{2} = \frac{1}{2}$$
 mole

Moles of
$$C_2H_4$$
 to be burnt = $\frac{14}{28} = \frac{1}{2}$ mole.

$$:$$
 1 mole of C_2H_4 requires 3 moles of O_2 for combustion

∴
$$\frac{1}{2}$$
 mole C_2H_4 requires $\frac{3}{2}$ mole O_2

Mass of oxygen =
$$3/2 \times 32 = 48$$
 g

22. (2):
$$\lambda = \frac{h}{mv}$$

$$\therefore mv = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34}}{0.33 \times 10^{-9}} = 2.007 \times 10^{-24} \text{ kg m sec}^{-1}$$

23. (200):
$$N_1V_1(Acid) = N_2V_2(Base)$$

$$\frac{1}{2} \times 100 = \frac{1}{4} \times V_2$$
; $V_2 = 200 \text{ mL}$

24. (0): We know,
$$\Delta x$$
. $\Delta p = \frac{h}{4\pi}$

$$\Delta x = \frac{h}{4\pi} \times \frac{1}{\infty} = 0$$

25. (1259.52): We know,
$$E_n = -\frac{1312}{n^2} \text{ kJ mol}^{-1}$$

For H-atom
$$\Delta E = E_5 - E_1 = -\frac{1312}{5^2} - \left(-\frac{1312}{1^2}\right)$$

$$= 1312 \left[\frac{1}{1^2} - \frac{1}{5^2} \right] = 1312 \times \frac{24}{25} = 1259.52 \text{ kJ mol}^{-1}$$

Thus, energy required = $1259.52 \text{ kJ mol}^{-1}$



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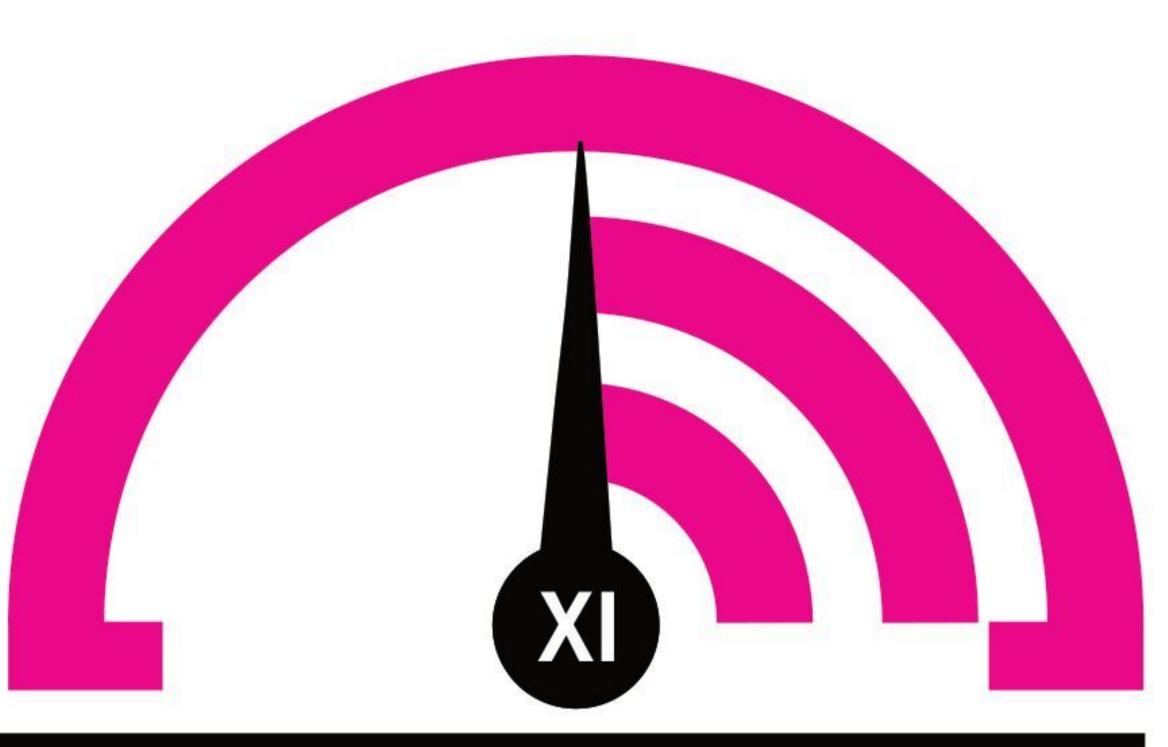
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MONTHLY TEST



his specially designed column enables students to self analyse their extent of understanding the specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

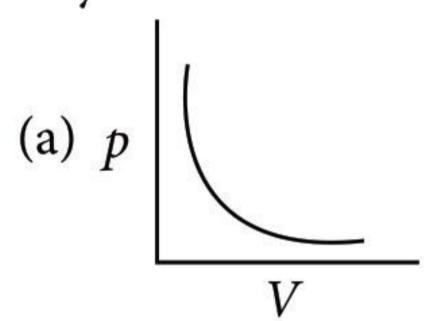
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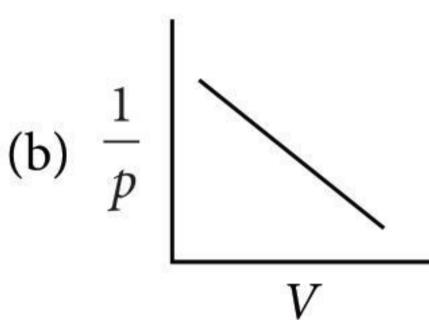
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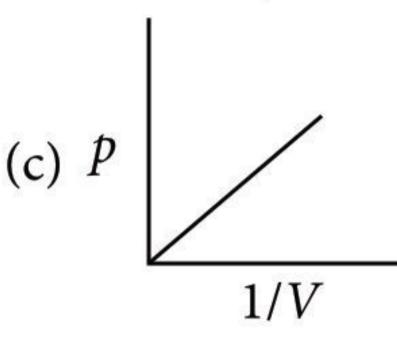
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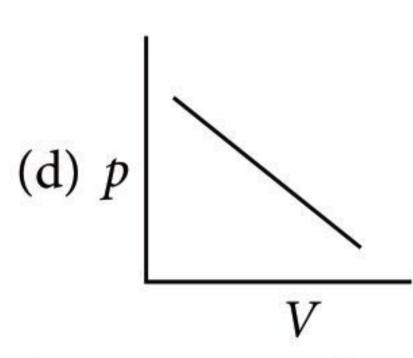
Only One Option Correct Type

Which of the following curve does not represent Boyle's law?









- 2. The behaviour of a real gas is usually depicted by plotting compressibility factor Z versus p at a constant temperature. At high temperature and high pressure, Z is usually more than one. This fact can be explained by van der Waals' equation when
 - (a) the constant *a* is negligible and not *b*
 - (b) the constant *b* is negligible and not *a*
 - (c) both the constants *a* and *b* are negligible
 - (d) both the constants *a* and *b* are not negligible.
- 3. A system changes its state from A to B. The resulting change of entropy will be a definite quantity
 - (a) when the change is reversible
 - (b) when the change is irreversible
 - (c) when the change is isothermal
 - (d) always irrespective of the manner in which the change is brought about.
- 4. A scientist needs a refrigeration machine to maintain temperature of -13° C for certain chemical process. How much work must be performed on the system during each cycle of its operation, if 3000 J

- of heat is to be withdrawn from -13° C reservoir and discharged to the room at +27° C? Assume that the machine operates at 100 % of its theoretical efficiency.
- (a) 65000 J (b) 3000 J (c) 154 J
- Volume of the air that will be expelled from a vessel of 300 cm³ when it is heated from 27° C to 37° C at
- the same pressure will be (a) 310 cm^3
 - (b) 290 cm^3
- (c) 10 cm^3
- (d) 37 cm^3
- The heats of neutralization of CH₃COOH, HCOOH, HCN and H_2S are -13.2, -13.4, -2.9 and -3.8 kcal per equivalent respectively. The correct increasing order of acid strength is
 - (a) $HCOOH < CH_3COOH < H_2S < HCN$
 - (b) $HCN < H_2S < CH_3COOH < HCOOH$
 - (c) $HCOOH < CH_3COOH < HCN < H_2S$
 - (d) $CH_3COOH < H_2S < HCN < HCOOH$
- Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of dipoles possess 'partial charges'. The partial charge is
 - (a) more than unit electronic charge
 - (b) equal to unit electronic charge
 - (c) less than unit electronic charge
 - (d) double the unit electronic charge
- The value of a van der Waals' constant 'a' for gases O₂, N₂, NH₃ and CH₄ are 1.360, 1.390, 4.170 and 2.253 litre² atm mol⁻² respectively. The gas which can most easily be liquefied is
- (b) N_2
- (c) NH_3
- 9. A particular state of system is arrived at starting from a given state in two different ways (1) following reversible path and (2) irreversible path. Which of the following relation would be correct if the processes are isothermal?

- (a) $\Delta S_{rev} \neq \Delta S_{irrev}$ (b) $\Delta q_{rev} = \Delta q_{irrev}$ (c) $\Delta S_{rev} = \Delta S_{irrev} = \frac{\Delta q_{rev}}{T}$
- (d) $\Delta S_{irrev} = \frac{\Delta q_{irrev}}{T} \neq \Delta S_{rev}$
- 10. Average kinetic energy of CO_2 at 300 K is E. The average kinetic energy of N₂ at the same temperature will be
 - (a) E (b) $\frac{E}{2}$ (c) $\frac{44E}{2}$ (d) $\frac{28E}{44}$

- 11. Given that $C + O_2 \rightarrow CO_2$; $\Delta H^{\circ} = -a \text{ kJ}$ $2CO + O_2 \rightarrow 2CO_2$; $\Delta H^{\circ} = -b \text{ kJ}$ The heat of formation of CO is
 - (a) b-2a (b) $\frac{2a-b}{2}$ (c) $\frac{b-2a}{2}$ (d) 2a-b
- 12. For the equilibrium,

 $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ at 1 atm and 298 K,

- (a) standard free energy change is equal to zero $(\Delta G^{\circ} = 0)$
- (b) free energy change is less than zero ($\Delta G < 0$)
- (c) standard free energy change is less than zero $(\Delta G^{\circ} < 0)$
- (d) standard free energy change is more than zero $(\Delta G^{\circ} > 0)$.

Assertion & Reason Type

Directions: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- If assertion is true but reason is false.
- 13. Assertion: The compressibility factor for H_2 and He is greater than one.

Reason: The compressibility factor for H₂ and He can be derived from van der Waals' equation.

14. Assertion: A non-spontaneous endothermic reaction at room temperature may be spontaneous at high temperature.

Reason: At high temperature the value of $T\Delta S$ becomes more than ΔH .

15. Assertion: Liquid surfaces always tend to have minimum surface area.

Reason: Small liquid drops have spherical shape.

JEE MAIN / JEE ADVANCED Only One Option Correct Type

16. The mass of molecule A is half the mass of molecule B whereas the rms speed of A is twice the rms speed of B. If two samples of *A* and *B* contain same number of

molecules, what will be the ratio of pressure of A to that of B in samples in separate containers of equal volume?

- (a) 8 (b) 4 (c) 2 (d) 1/2
- 17. Adiabatic reversible expansion of a gas is represented by

(a)
$$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{p_2}{p_1}\right)^{(1-\gamma)}$$
 (b) $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{p_1}{p_2}\right)^{(1-\gamma)}$

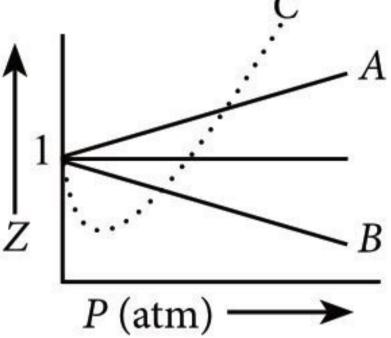
- (c) $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{p_2}{p_1}\right)^{\gamma-1}$ (d) All of the above
- 18. Which of the following statements is false?
 - (a) Avogadro Number = 6.02×10^{23}
 - (b) The relationship between average velocity and root mean square velocity u is $\bar{\nu} = 0.897u$.
 - (c) The mean kinetic energy of an ideal gas is independent of the pressure of the gas.
 - (d) The root mean square velocity of the gas can be calculated by the formula $(3RT/M)^{1/2}$.
- 19. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct?
 - (a) $(T_f)_{irrev} > (T_f)_{rev}$
 - (b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
 - (c) $(T_f)_{rev} = (T_f)_{irrev}$
 - (d) $T_f = T_i$ for both reversible and irreversible processes.

More than One Option Correct Type

20. The given graph represents the variation of Z

(compressibility

versus p, for three real gases A, B and C. Identify the correct statements.



- (a) For the gas A, a = 0 and its dependence on *p* is linear at all pressure.
- (b) For the gas B, b = 0 and its dependence on p is linear at all pressure.
- (c) For the gas C, which is typical real gas for which neither a nor b = 0. By knowing the minima and the point of intersection, with Z = 1, a and b can be calculated
- (d) At high pressure, the slope is positive for all real gases.
- 21. Which are extensive property among the given options?
 - (a) *V*
- (b) *T*
- (c) Mass
- (d) *P*

- 22. Which of following statements are correct?
 - (a) Average velocity of molecules of a gas in a container is zero.
 - (b) All molecules in a gas are moving with the same speed.
 - (c) If an open container is heated from 300 K to 400 K, the fraction of air which goes out with respect to originally present is 1/4.
 - (d) If compressibility factor of a gas at STP is less than unity then its molar volume is less than 22.4 L at STP.
- 23. For which of the following reaction, change of enthalpy equals the change in internal energy?
 - (a) $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$
 - (b) $PCl_{5(g)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$
 - (c) $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$
 - (d) $C_{(s)} + O_{2(g)} \to CO_{2(g)}$

Integer / Numerical Value Type

- 24. Calculate the entropy change (in $J K^{-1} \text{ mol}^{-1}$) involved in conversion of one mole of liquid water at 373 K to vapour at the same temperature (latent heat of vaporisation of water $\Delta_{\text{vap}}H = 2.257 \text{ kJ g}^{-1}$).
- 25. Calculate the partial pressure (in atm) of the He gas in a 10 litre cylinder which contains 0.4 g He, 1.6 g O₂ and 1.4 g of N₂ at 27 °C. Assume ideal behavior of gases, R = 0.0821 atm lit K⁻¹ mol⁻¹.
- 26. From the following data, calculate the enthalpy change in (kJ mol⁻¹) for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_{2(g)}$, $H_2O_{(l)}$ and propene_(g) are -393.5, -285.8 and 20.42 kJ mol⁻¹ respectively. The enthalpy of isomerization of cyclopropane to propene is $-33.0 \text{ kJ mol}^{-1}$.

Comprehension Type

An intimate mixture of Fe₂O₃ and Al is used in solid fuel rocket.

 $\Delta H_{\text{Al}_2\text{O}_3} = 399.0 \text{ kcal}, \ \Delta H_{\text{Fe}_2\text{O}_3} = 199.0 \text{ kcal}$ Density of Fe₂O₃ and Al are 5.2 g mL⁻¹ and 2.7 g mL⁻¹ respectively.

- 27. The fuel value per g of the mixture is

 - (a) $0.9346 \text{ kcal g}^{-1}$ (b) $0.7821 \text{ kcal g}^{-1}$
 - (c) $0.6281 \text{ kcal g}^{-1}$ (d) $0.5281 \text{ kcal g}^{-1}$
- 28. The fuel value per mL of the mixture is

 - (a) $3.94 \text{ kcal mL}^{-1}$ (b) $2.81 \text{ kcal mL}^{-1}$

 - (c) $3.25 \text{ kcal mL}^{-1}$ (d) $2.17 \text{ kcal mL}^{-1}$

Matrix Match Type

29. Match List I (Equations) with List II (Types of processes) and select the correct option.

	List I		List II		
A.	$K_p > Q$	p.	Non-spontaneous		
B.	$\Delta G^{\circ} > O$	q.	Equilibrium		
C.	$K_p = Q$	r.	Spontaneous and endothermic		
D.	$T > \Delta H/\Delta S$	s.	Spontaneous		

- (a) A (p), B (q), C (r), D (s)
- (b) A (r), B (p), C (q), D (s)
- (c) A (s), B (p), C (q), D (r)
- (d) A (q), B (p), C (s), D (r)
- 30. Match the List I (Graphs of ideal gas) with List II (Their co-ordinates) and select the correct option.

Graj	List I Graphical representation		List II y co-ordinates
(i)		(A)	pV vs V
(ii)		(B)	p vs V
(iii)		(C)	p vs 1/V

- (a) (i) \rightarrow (B), (ii) \rightarrow (A), (iii) \rightarrow (C)
- (b) (i) \rightarrow (B), (ii) \rightarrow (C), (iii) \rightarrow (A)
- (c) (i) \rightarrow (A), (ii) \rightarrow (C), (iii) \rightarrow (B)
- (d) (i) \rightarrow (C), (ii) \rightarrow (A), (iii) \rightarrow (B)



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EXCELLENT WORK!

You are well prepared to take the challenge of final exam.

No. of questions attempted

90-75% GOOD WORK!

You can score good in the final exam.

74-60% SATISFACTORY!

You need to score more next time.

Marks scored in percentage

No. of questions correct

< 60% NOT SATISFACTORY! Revise thoroughly and strengthen your concepts.

AROMATIC HYDROCARBONS

Aromatic hydrocarbons are also known as arenes. Benzene is the simplest aromatic hydrocarbon. Benzene ring is a six membered ring containing carbon atoms linked to each other with alternate single and double bonds. Arenes contain higher proportion of carbon as compared to the aliphatic hydrocarbons and constitute a unique class of unsaturated hydrocarbons.

Benzenoids

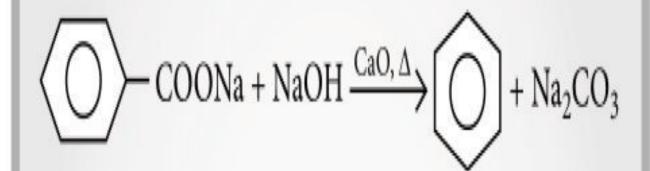
Aromatic hydrocarbons containing a benzene ring are called benzenoids. Their general formula is C_nH_{2n-6m} , (where, n = no. of C-atoms, m = no. of rings.)

Preparation

Cyclic polymerisation of ethyne

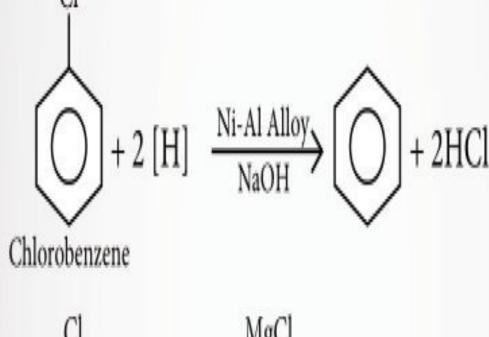
$$3CH \equiv CH \xrightarrow{\text{Red hot Fe-tube}} \bigcirc$$

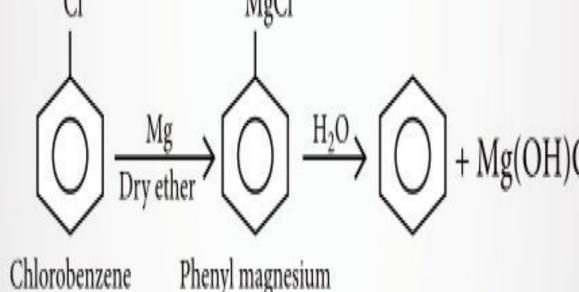
Decarboxylation of aromatic acids



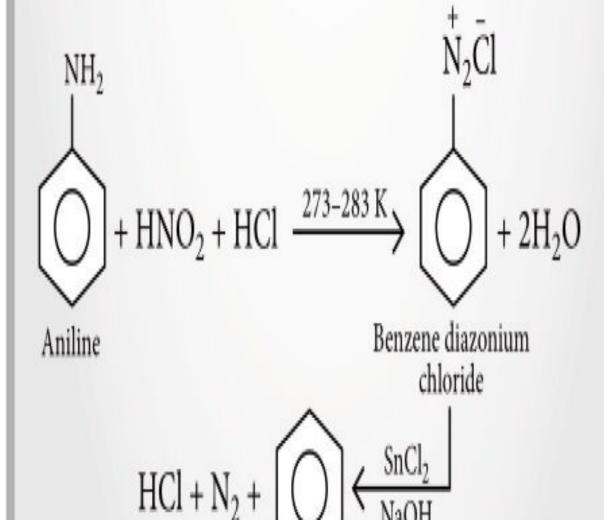
Reduction of phenol

From chlorobenzene

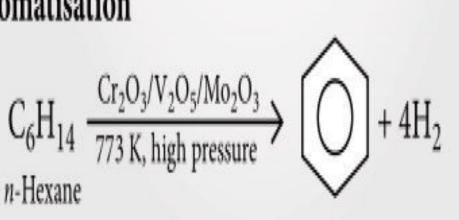




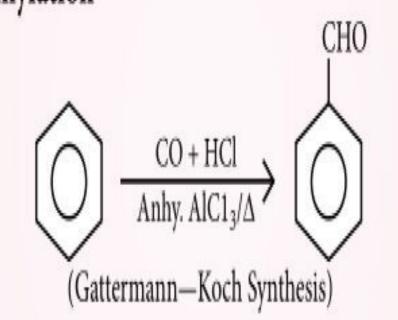
From aniline



Aromatisation

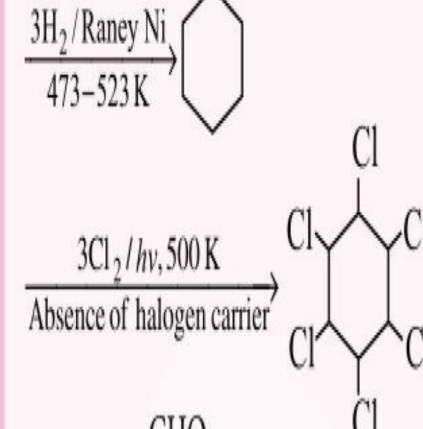


Formylation



Properties

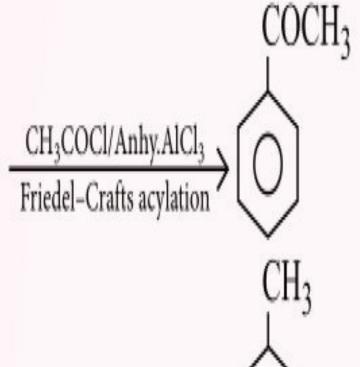
Addition reactions

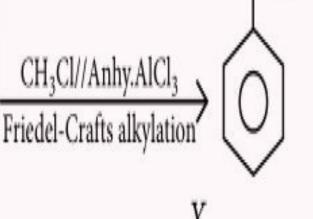


$$\begin{array}{c}
CHO \\
\xrightarrow{O_3} & 3 \\
\hline
Zn/H_2O
\end{array}$$
CHO

CHO

Electrophilic substitution reactions

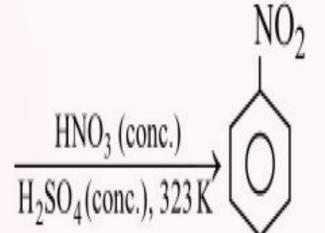




$$\frac{X_2/\text{Anhy.Al}X_3}{310-320 \text{ K, dark}} \bigcirc (X = \text{Cl, Br, I})$$

$$SO_3H$$

$$\frac{H_2SO_4 \text{ (Fuming)}}{3220 \text{ K}} \bigcirc (SO_3H)$$



Oxidation reactions

$$\xrightarrow{150_2} 12\text{CO}_2 + 6\text{H}_2\text{O}$$

(Complete oxidation)

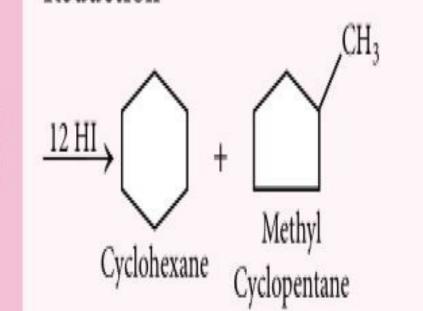
$$\xrightarrow{9/2O_2/V_2O_5,773 \text{ K}} CHCO \searrow 0$$

$$CHCO \searrow 0$$

$$CHCO \searrow 0$$

(Controlled oxidation)

Reduction



AROMATIC COMPOUNDS

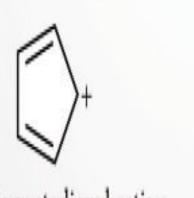
- Planar, cyclic and completely conjugated
- Contains $(4n + 2)\pi$ -electrons, (Huckel's Rule) (where, n = 0, 1, 2...
- On ring closure, the π -electron energy of an open chain polyene decreases (Benzene), Cyclopropenyl annulene cyclopentatrienylcation (tropylium ion),

cyclopropenyl cation, etc.

(Aromatic)

Anti-aromatic Compounds

- Planar, cyclic and completely conjugated
- Contains $4n\pi$ -electrons, (where, n = 0, 1, 2 ...)
- On ring closure, the π -electron energy increases e.g., cyclopentadienyl cation





Cyclopentadienyl cation (Anti-aromatic)

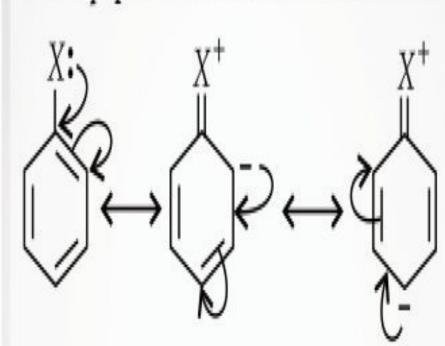
Cyclopropenyl anion (Anti-aromatic)

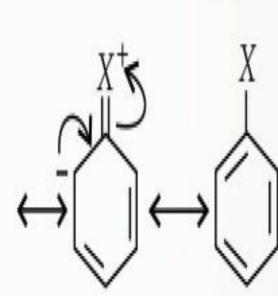
Directive Influence of Substituents

The ability of a group already present in the benzene ring to direct the incoming group to a particular position is called the directive influence of groups.

o, p-directive

Groups with positive mesomeric effect (+M) increases electron density at *o*-and *p*-positions due to delocalisation.



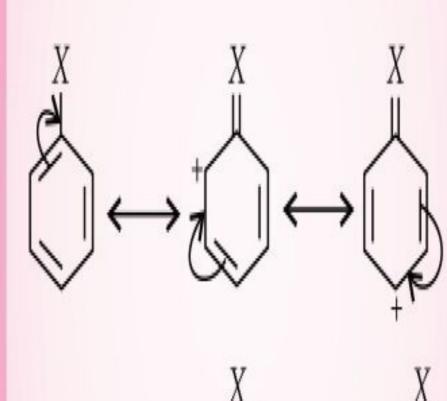


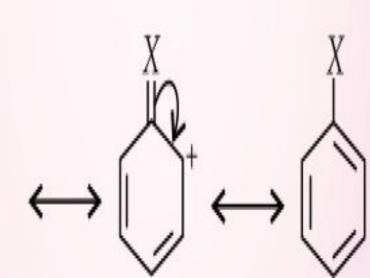
(Here, X may be $-CH_3$, $-C_2H_5$, $-OCH_3$, $-NH_2$, -NHR, $-NHCOCH_3$, -OH, -F, -Cl, -Br, -I.

Thus, electrophile attacks on o- and p-positions because these are electron rich positions.

m-directive

Groups with negative mesomeric effect (-M) decreases electron density on o- and p-positions, so electrophile will attack on *m*-position.





(Here, X may be $-NO_2$, -CHO, -COR, -COOH, -COOR, $-SO_3H$, -CN.

Non-aromatic Compounds

- Non-planar, non-cyclic and not completely conjugated
- If, on ring closure, the π -electron energy remains the same

(Non-aromatic) e.g., Alkanes, alkenes and 1, 3, 5-cycloheptatriene

Cyclooctatetraene

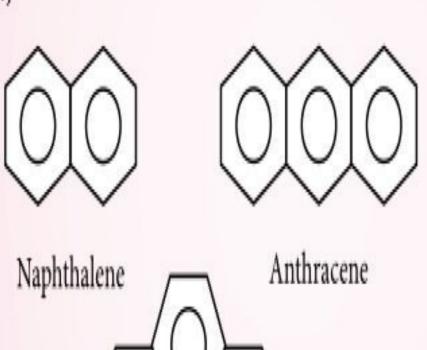
(tub-shaped)

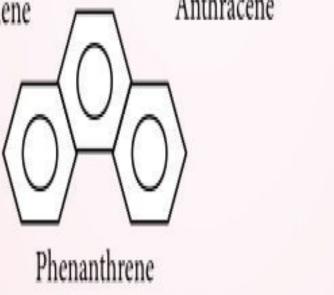
Non-Benzenoids

 Do not contain benzene ring e.g., Azulene, tropolone, pyrrole, etc.

Polynuclear Hydrocarbons

Compounds having more than one aromatic ring are known as polynuclear hydrocarbons.





Carcinogenicity & Toxicity

- PAH's (Polycyclic Aromatic Hydrocarbons) generally have a low degree of acute toxicity to humans.
- The most significant end point of PAH toxicity is cancer.
- Increased incidences of lung, skin and bladder cancers are associated with occupational exposure to PAHs.
- PAH's toxicity is very structurally dependent, with isomers (PAHs with the same formula and number of rings) varying from being non-toxic to being extremely toxic.
- One PAH compound, benzo[a]pyrene, is notable for being the first chemical carcinogen to be discovered (and is one of many carcinogens found in cigarette smoke).
- High prenatal exposure to PAH is associated with lower IQ and childhood asthma.



Warm-up!

Chapterwise practice questions for CBSE Exams as per the latest pattern and reduced syllabus by CBSE for the academic session 2022-23.

Series-2

Classification of Elements and Periodicity in Properties | **Chemical Bonding and Molecular Structure**

Time Allowed: 3 hours Maximum Marks: 70

GENERAL INSTRUCTIONS

General Instructions: Read the following instructions carefully.

- There are 33 questions in this question paper. All questions are compulsory.
- Section A: Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
- Section B: Q. No. 17 to 25 are short answer questions and carry 2 marks each.
- Section C: Q. No. 26 to 30 are short answer questions and carry 3 marks each.
- Section D: Q. No. 31 to 33 are long answer questions carrying 5 marks each. (e)
- There is no overall choice. However, internal choices have been provided.
- Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

Read the passage given below and answer the following questions:

1. Molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. Molecular orbitals are formed by the addition or subtraction of wave functions of the atomic orbitals. Filling of electrons in molecular orbitals takes place in accordance with Aufbau's principle, Hund's rule and Pauli's exclusion principle.

Energy order for molecular orbitals upto N_2 :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z$$

 $< (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

Energy order for molecules beyond N_2 :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

Bond order: The number of covalent bonds formed in a molecule is called its bond order.

Bond order (B.O.) =
$$\frac{1}{2} (N_b - N_a)$$

where, N_b is number of electrons present in bonding molecular orbital and N_a is number of electrons present in anti bonding molecular orbital.

The following questions are multiple choice questions. Choose the most appropriate answer.

- The number of electrons that are paired in oxygen molecule is
 - (a) 16
- (b) 12
- (c) 14
- (d) 8
- (ii) Which of the following is non-existent according to molecular orbital theory?
 - (a) H_2^-
- (b) O_2^-
- (c) He_2
- (d) O_2^+

The molecular species having highest bond order is (b) O_2^- (c) O_2^+ (d) O_2^{2-} (a) O_2

- (iii) According to MO theory which of the lists ranks the nitrogen species in terms of increasing bond order?

 - (a) $N_2^{2-} < N_2^{-} < N_2$ (b) $N_2 < N_2^{2-} < N_2^{-}$

 - (c) $N_2 < N_2^{2-} < N_2$ (d) $N_2 < N_2 < N_2^{2-}$

- (iv) The molecule having bond order 3 is
 - (a) H_2
- (b) N_2
 - (c) O₂
- $\mathrm{He}_2^{\mathrm{T}}$ (d)

Read the passage given below and answer the following questions:

- 2. In modern periodic table, the elements have been arranged in the increasing order of atomic number. After a regular interval, element with similar properties are repeated. Ionisation enthalpy of the element is the energy required to remove an electron from an isolated gaseous atom in its ground state it can be represented as:
 - $M_{(g)} + I.E. \longrightarrow M_{(g)}^+ + e^-$

The order of successive ionisation energy of an element can be written as : $I.E_3 > I.E_2 > I.E_1$

In these questions, Q. No. (i)-(iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- (i) Assertion: Ionization enthalpy is the energy released to remove an electron from an isolated gaseous atom in its ground state.

Reason: Element has a tendency to lose the electron to attain the stable configuration.

(ii) Assertion: Ionization enthalpy is always negative. Reason: Energy is always absorbed when electrons are removed.

OR

Assertion: Second ionization enthalpy will be higher than the first ionization enthalpy.

Reason: Ionization enthalpy is a quantitative measure of the tendency of an element to lose electron.

(iii) Assertion: First ionization enthalpy of boron is slightly less than that of beryllium.

Reason: Ionization enthalpy increases as we go across the period.

(iv) Assertion: Nuclear charge does not affect the ionization potential of the atom.

increase in nuclear charge.

Following questions (Q. No. 3-11) are multiple choice questions carrying 1 mark each:

- Which among the following is an electron deficient compound?
 - (a) NF_3
- (b) PF_3
- BF_3 (c)
- (d) AsF_3

OR

Which of the following is least ionic?

- (a) AgCl
- (b) KCl
- BaCl₂ (c)
- (d) CaCl₂
- Which of the following has covalent as well as ionic bond?
 - (a) NaCl
- (b) NaOH (c) H_2O

- The compound which contains both ionic and covalent bonds is
 - (a) CH_{4}
- (b) H_2
- - (c) KCN
- (d) KCl
- Which one of the following is a non polar molecule?
 - (a) CCl_4
- (b) CHCl₃
- (c) CH_2Cl_2
- (d) CH₃Cl

OR

In which of the following molecules is the covalent bond is most polar?

- (a) HI
- (b) HBr
- HCl (c)
- (d) H_2
- What is the correct order of decreasing first ionization enthalpies?
 - (a) F > O > N > C
- (b) C > N > O > F
- (c) F > N > O > C
- (d) F > N > C > O
- Which of the following decreases down the group in periodic table?
 - (a) Basic nature of oxides
 - (b) Non-metallic character
 - (c) Electronegativity
 - (d) Both (b) and (c)
- The successive ionisation energies in kJ/mol of an element P are 740, 1500, 7000, 10500, 13600, 18000 and 21700. Which ion is the most likely to be formed when *P* reacts with chloride?
 - (a) P^{2-}
- (b) P^+
- (c) P^{2+}
- (d) P^{3+}

OR

Aqueous solutions of two compounds M–O–H and M'-O-H have been prepared in two different beakers. If the electronegativity of M = 3.5, M' = 1.72, O = 3.0 and H = 2.1, then the solutions respectively are

- (a) acidic, acidic
- acidic, basic
- (c) basic, basic
- basic, acidic.
- **Reason:** Ionisation potential increases with 10. The element which has lowest ionisation potential is
 - (a) Cs
- (b) Li
- (c) Na

Identify the least stable ion amongst the following.

- (a) Li⁻
- (b) Be⁻ (c) B⁻

- 11. The second ionisation energy is highest for
 - (a) Mg
- (b) Al
- (c) Na
- (d) Si

In the following questions (Q. No. 12 - 16) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- 12. **Assertion**: Bond angle of H_2S is greater than H_2O . Reason: Electronegativity of the central atom increases, bond angle increases.
- 13. Assertion: In NH₃, N is sp^3 hybridised, but angle is found to be 107°.

Reason: The decrease in bond angle is due to repulsion between the lone pair on nitrogen and bond pair between N and H.

OR

Assertion: BF₃ molecule has zero dipole moment. **Reason**: F is electronegative and B – F bonds are polar in nature.

- 14. Assertion: Shape of NH₃ molecule is tetrahedral. **Reason**: In NH₃, nitrogen is sp^3 hybridised.
- 15. Assertion: Shielding effect increases as we go down the group.

Reason: More is the number of electrons in the penultimate shell, more is shielding.

16. Assertion: The highest *I.E.* in a period is shown by noble gas.

Reason: Noble gases are at the extreme right of the period.

SECTION - B

The following questions, Q. No. 17-25 are short answer type and carry 2 marks each.

17. Define ionization enthalpy. Why is second ionization enthalpy always greater than the first ionization enthalpy?

OR

Explain why the electron gain enthalpy of fluorine is less negative than that of chlorine.

- (a) ClF₃ XeF_4 **(b)**
- 19. Can a π bond be formed without the formation of a sigma (σ) bond? How many σ and π bonds are formed in acetylene?

18. Draw the shapes of following molecules using

OR

Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

20. Explain with reason:

VSEPR theory:

- (a) Mg^{2+} ion is smaller than O^{2-} ion, although both are isoelectronic.
- (b) Why Be and Mg atoms do not impart colour to the flame?

OR

Account for the following:

- (a) The first ionization enthalpy of magnesium is higher than that of aluminium.
- (b) The first element of all the groups show anomalous behaviour.
- 21. The increasing order of reactivity among group 1 elements is Li < Na < K < Rb < Cs whereas that among group 17 elements is F > Cl > Br > I. Explain.
- 22. Nitrogen has positive electron gain enthalpy whereas oxygen has negative. However, oxygen has lower ionisation enthalpy than nitrogen. Explain.
- 23. Explain why cations are smaller and anions are larger in radii than their parent atoms.
- 24. Predict the formula of the binary compound formed by the combination of the following pairs of elements:
 - (i) Magnesium and nitrogen
 - (ii) Silicon and oxygen
- 25. Why is sigma bond stronger than π -bond? Explain.

SECTION - C

- Q. No. 26-30 are short answer type II carrying 3 marks each.
- **26.** Describe the shapes of sp, sp^2 and sp^3 hybrid orbitals with the help of an example.

OR

Describe the shapes of the following hybrid orbitals with example.

- (a) sp^2
- **(b)** sp^3d^2 **(c)** sp^3d
- 27. What are the factors due to which the ionisation enthalpy of the main group elements tends to decrease down the group? (Explain any two).

The electron gain enthalpy of bromine is 3.36 eV. How much energy in kcal is released when 8 g of bromine is completely converted to Br ions in the gaseous state?

 $(1 \text{ eV} = 23.06 \text{ kcal mol}^{-1}).$

- 28. Explain the geometry of SF_6 molecule, by writing electronic configuration of sulphur and showing hybridisation involved.
- 29. Give reasons for the following:
 - (a) Covalent bonds are directional bonds while ionic bonds are non-directional.
 - (b) Water molecule has bent structure whereas carbon dioxide molecule is linear.
 - (c) Ethyne molecule is linear.
- **30.** (i) What is the oxidation state and covalency of Al in $[AlCl(H_2O)_5]^{2+}$?
 - (ii) Which out of the following will have the most negative electron gain enthalpy and which have the least negative? P, S, Cl and F.

SECTION - D

Q. No. 31-33 are long answer type carrying 5 marks each.

31. Briefly describe the valence bond theory of covalent bond formation by taking an example of hydrogen. How can you interpret energy changes taking place in the formation of dihydrogen?

OR

- (i) Which of the following pair will have the higher value of the property mentioned? Give reason.
 - LiF, ClF₃ (Ionic character)
 - O_2 , F_2 (Bond order)
 - NH₃, NF₃ (Dipole moment)
- (ii) Draw the Lewis structure of H₂S.
- (iii) Which has higher bond angle and why: NO₂⁺, NO_2^- ?
- 32. Arrange the following in increasing order of the property indicated:
 - (i) F, Cl, Br and I (electron gain enthalpy)
 - (ii) Pb, Pb²⁺ and Pb⁴⁺ (size)
 - (iii) I₂, F₂, Br₂ and Cl₂ (reactivity)
 - (iv) SiO₂, P₂O₅, SO₃ and Cl₂O₇ (acidic nature)
 - (v) C, N, O and F (2nd ionisation enthalpy)

Give the name and symbol for each of the atoms which have the ground state electronic configurations in their outer shells:

- (b) $3s^2 3p^6 4s^2$ (d) $5s^2 5p^2$
- (a) $3s^23p^5$ (c) $3s^23p^63d^64s^2$ (e) $5s^25p^6$
- 33. Which of the following molecules will have the same shape as SO_2 ?
 - SnCl₂, CO₂, BeH₂.
 - (ii) Using VSEPR theory, identify the type of hybridisation and draw the structure of OF₂. What are the oxidation states of O and F?

OR

- (i) What is the decreasing order of repulsion of various electron pairs? l.p.-l.p., b.p.-b.p., l.p.-b.p.
 - (ii) ClF₃ is a T-shape molecule while NF₃ has a trigonal pyramidal shape. Explain.
- (iii) Why is it that in the SF₄ molecule, the lone pair of electrons occupies an equitorial position in the overall trigonal bipyramidal arrangement in preference to the axial position?

SOLUTIONS

1. (i) (c):
$$O_2 \to KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$$

 $\pi^* 2p_x^1 = \pi^* 2p_y^1$

Total paired electrons are 14.

(ii) (c): He₂ (4 electrons):
$$\sigma 1s^2 \sigma^* 1s^2$$

B.O. =
$$\frac{2-2}{2}$$
 = 0

OR

(c): O₂ (16 electrons):
$$KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2$$

 $\pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$

$$O_2$$
: B.O. = $\frac{8-4}{2}$ = 2; O_2^- : B.O. = $\frac{8-5}{2}$ = 1.5

$$O_2^+$$
: B.O. = $\frac{8-3}{2}$ = 2.5; O_2^{2-} : B.O. = $\frac{8-6}{2}$ = 1

- (iii)(a)
- (iv) (b): B.O. of $N_2 = 3$.
- 2. (i) (d): Ionisation enthalpy is the energy required to remove an electron from an isolated gaseous atom in its ground state. Every element does not have tendency to lose electrons.
- (ii) (d)

OR

(b)

(c): BF₃ has 6 electrons in the valence shell of B atom. As it has incomplete octet, so this is an electron deficient molecule.

(a): AgCl is a transition metal compound in which Ag is less electropositive. Hence, electronegativity difference is less and hence least ionic.

4. (b): $Na^{+}[O - H]^{-}$

5. (c): $K^{+}(C \equiv N)^{-}$

6. (a): A symmetrical molecule is non-polar even though it contains polar bonds. CCl_4 being symmetrical has zero resultant dipole moment and hence is non-polar since dipole moments summation of all the bonds present in the molecule is non-polar even Cl_4 being symmetrical Cl_4 and Cl_4 being symmetrical Cl_4 being symmetrical Cl_4 being symmetrical Cl_4 and Cl_4 being symmetrical Cl_4 being symmetrical Cl_4 being symmetrical Cl_4 and Cl_4 being symmetrical Cl_4 be

OR

(c)

7. (c): F > N > O > C

cancel each other.

8. (d)

9. (c): After losing two electrons, there is sudden huge increase in IE from 1500 to 7000 kJ/mol. It means that after losing two electrons, some stable configuration is achieved. So, element P forms P^{2+} ion.

OR

(b)

10. (a): Ionisation potential decreases down the group. Cs < K < Na < Li

OR

(b)

11. (c)

12. (d): Bond angle of H_2S (92.5°) < H_2O (104.5°). As the electronegativity of the central atom decreases, bond angle decreases. In the present case, S is less electronegative than oxygen. Thus, bond pairs in H_2S are more away from the central atom than in H_2O , and thus repulsive forces between bond pairs are smaller, producing smaller bond angle.

13. (a)

OR

(b) : BF_3 is sp^2 hybridised. Dipole moment is a vector quantity. The three bond moments give a net sum of zero, as the resultant of any two is equal and opposite to the third.

14. (d)

15. (a)

16. (b): Noble gases have completely filled electronic shells and thus have very stable electronic configuration. That is why, they have the highest *I.E.*

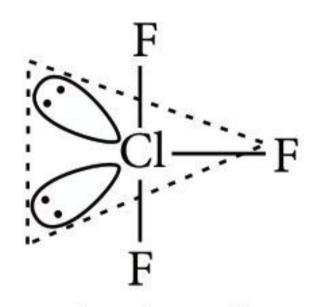
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17. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom.

OR

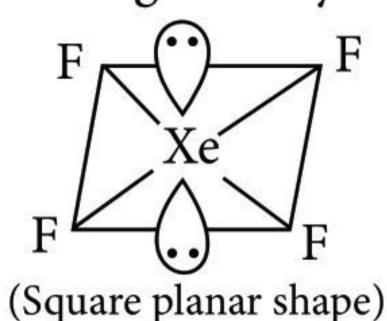
Due to small size of fluorine the incoming electron experiences repulsion from other electrons while in chlorine due to larger size of 3*p* orbital the repulsion is much less hence, electron gain enthalpy of chlorine is more negative than fluorine.

18. (a) ClF₃ has trigonal bipyramidal geometry.



(T-shaped)

(b) XeF₄ has octahedral geometry.



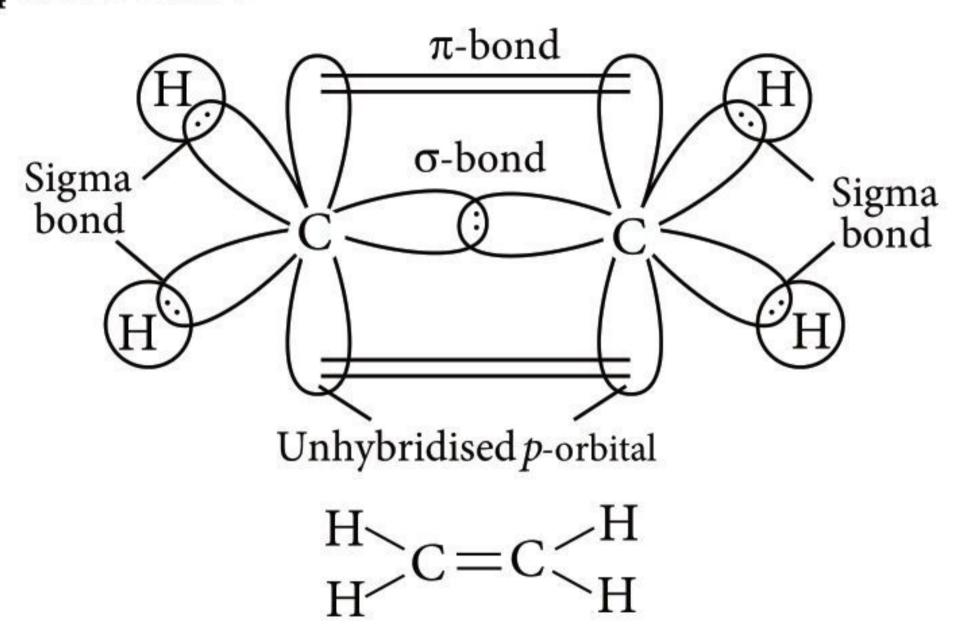
19. No, π bond cannot be formed without the formation of σ bond.

 C_2H_2 molecule: $H \stackrel{\sigma}{=} C \stackrel{2\pi}{=} C \stackrel{\sigma}{=} H$

 σ -bonds in acetylene = 1; π -bonds in acetylene = 2

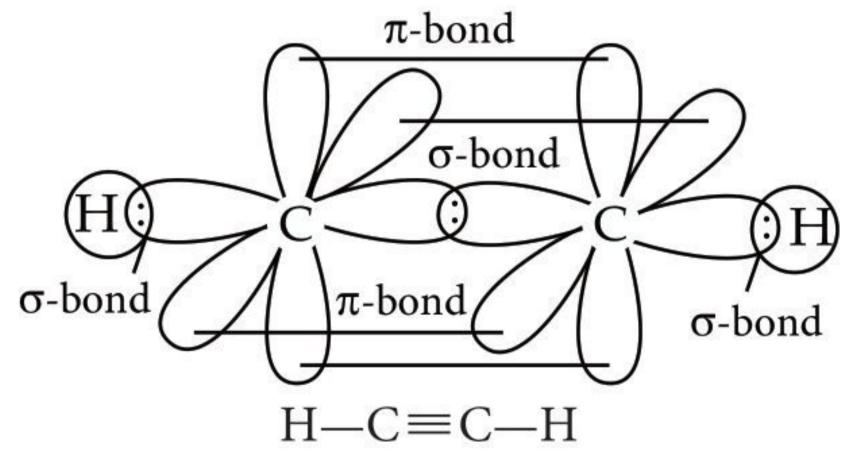
OR

C₂H₄ molecule:



(Formation of ethylene molecule)

C₂H₂ molecule:



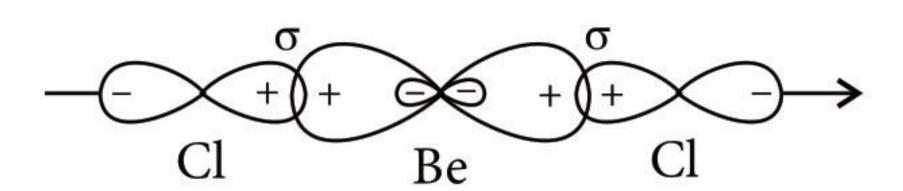
(Formation of acetylene molecule)

- 20. (a) As Z/e decreases, size increases and hence Mg^{2+} ion is smaller than O^{2-} ion.
- (b) Due to higher ionisation enthalpy Be and Mg do not impart colour to the flame.

- (a) Due to the presence of fully filled s-orbitals in Mg, it is difficult to pull out electron from stable configuration and therefore, Mg has higher first ionisation energy than Al.
- (b) First member of each group of s and p-block elements shows anomalous behaviour due to
- small size
- (ii) high ionisation enthalpy
- (iii) high electronegativity (iv) absence of d-orbitals.
- 21. The trend Li < Na < K < Rb < Cs is observed for chemical reactivity because upon descending the group the ionization energy of alkali metals decreases i.e., it is easy for them to lose an electron from their valence shell and attain the nearest stable noble gas configuration.

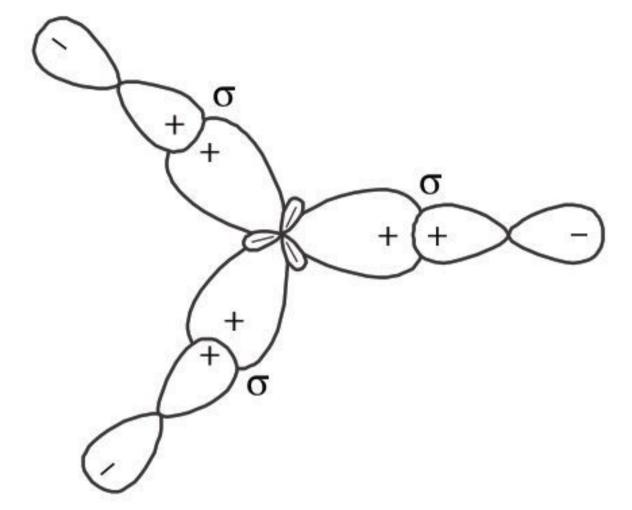
The trend F > Cl > Br > I is observed for chemical reactivity in halogens because the standard reduction potential decreases as we move down the group. F being the most electronegative readily accepts an e^- to complete its octet and hence is most reactive.

- 22. Nitrogen has positive electron gain enthalpy due to extra stability of half-filled p orbitals (N-2 s^2 2 p^3). Oxygen has four electrons in outermost shell (O- $2s^22p^4$) and it can easily accept two electrons hence, its electron gain enthalpy is negative. Due to stable configurations, ionisation enthalpy of nitrogen is higher than oxygen. It is easier to remove one electron from $2p^4$ as compared to $2p^3$.
- 23. A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge.
- 24. (i) Mg_3N_2 (ii) SiO₂
- 25. The strength of a bond depends upon the extent of overlapping. Since in the formation of σ -bond, overlapping is along the internuclear axis, therefore there is considerable overlapping. Hence, the σ -bond is a strong bond. On the other hand, in case of the formation of a π -bond, sideways overlapping takes place which is only to a small extent. Hence, π -bond is a weak bond.
- **26.** (i) *sp*-hybridisation: One 's' and one 'p' orbital of an atom intermix giving two *sp*-hybrid orbitals making an angle of 180° with each other.



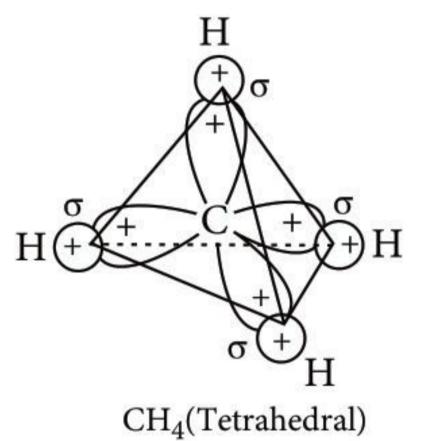
BeCl₂ molecule (linear)

(ii) sp^2 -hybridisation: One 's' and two 'p' orbitals of an atom intermix giving three sp^2 -hybrid orbitals, which are directed towards the corners of an equilateral triangle making an angle of 120° with each other.



BCl₃(Trigonal planar)

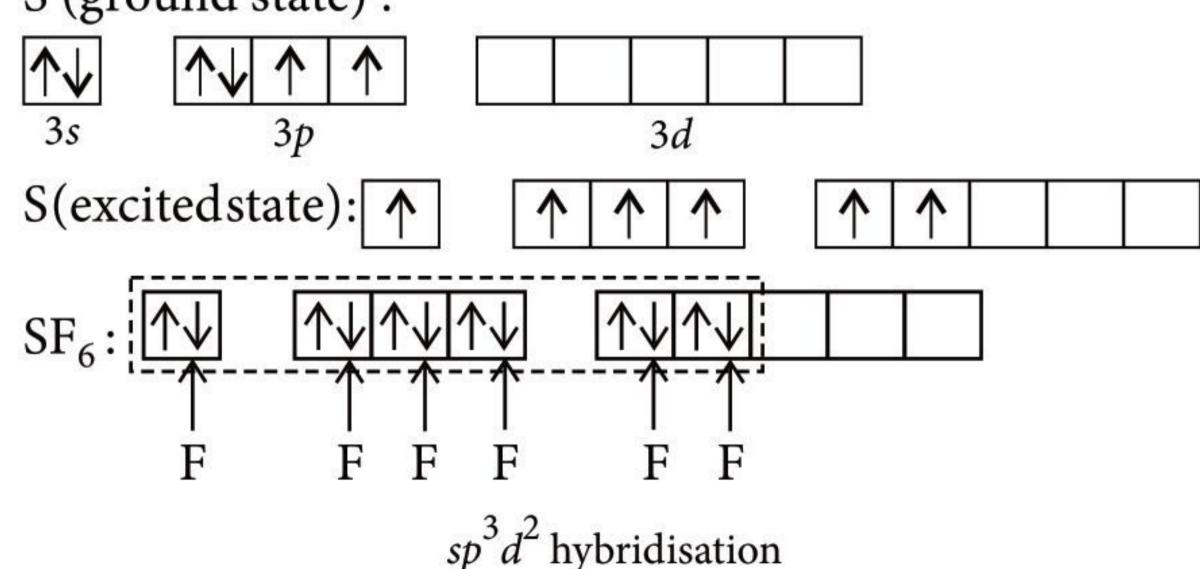
(iii) sp³-hybridisation: One 's' and three 'p' orbitals of an atom intermix giving four sp³-hybrid orbitals, which are directed towards the corners of a regular tetrahedron making an angle of 109°28'.



OR

- (a) sp^2 hybridisation: In BCl₃ B atom is sp^2 hybridised, it has trigonal planar shape and geometry. When one s and two p orbitals mix, then hybridisation involved is sp^2 .
- (b) sp^3d^2 hybridisation: In SF₆ the central sulphur atom has the ground state outer electronic configuration $3s^23p^4$. In the excited state the available six orbitals *i.e.*, one *s*, three *p* and two *d* are singly occupied by electrons. These orbitals hybridise to form six new sp^3d^2 hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF₆.

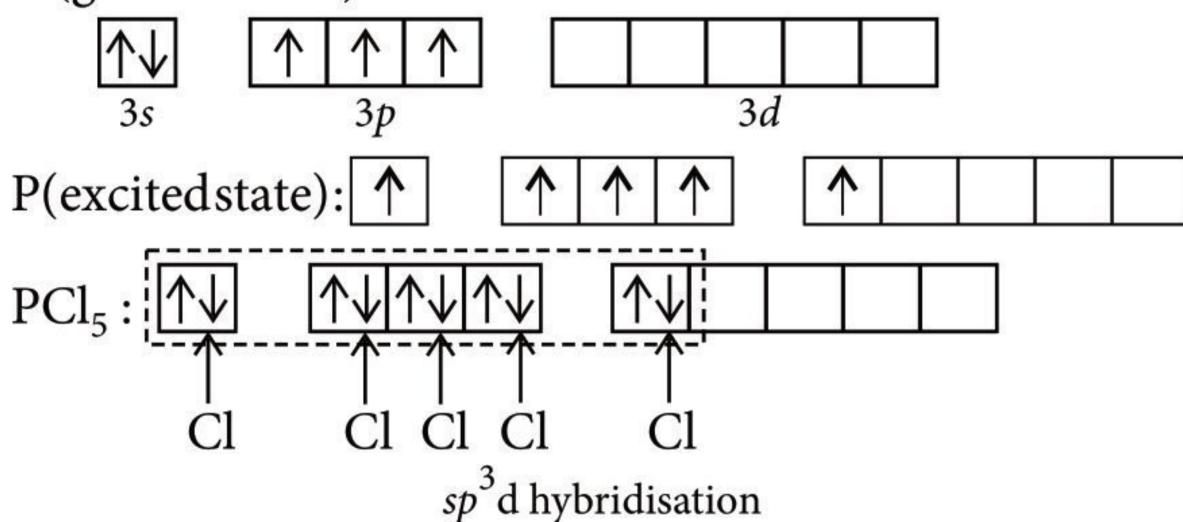
S (ground state):



The shape is octahedral.

(c) sp^3d hybridisation: The ground state and the excited state outer electronic configurations of phosphorus (Z = 15) are represented as:

P (ground state):



The shape is trigonal bipyramidal.

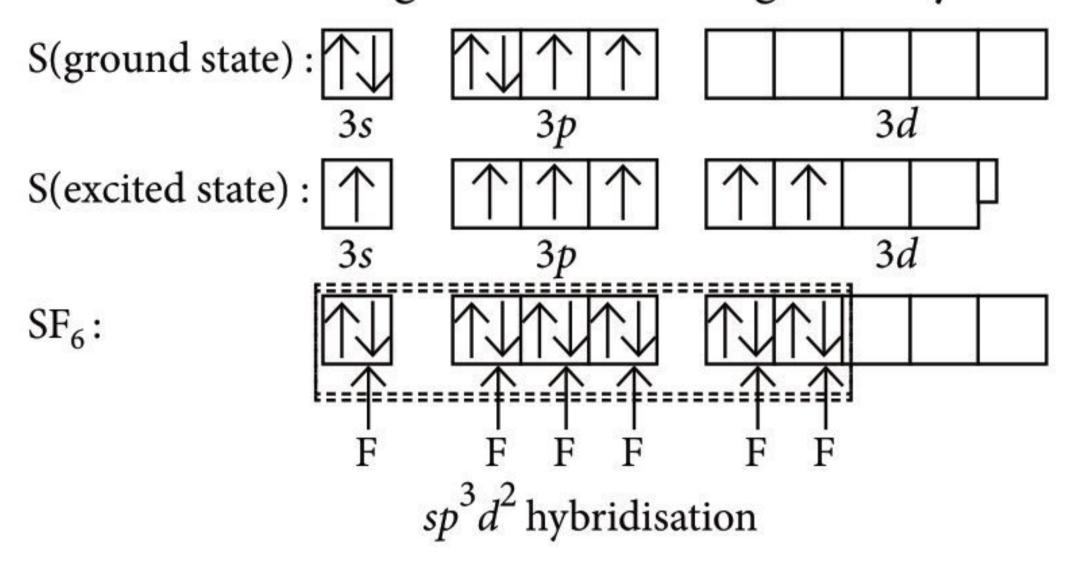
- 27. (i) Atomic size: On moving down the group the atomic size increases gradually due to the addition of one new principal energy shell. As a result, the distance of the valence electrons from the nucleus increases. Consequently the force of attraction by the nucleus for the valence electrons decreases and hence the ionization enthalpy decreases.
- (ii) Shielding effect: With the addition of new shells, the number of inner electron shells which shield the valence electrons from the nucleus increases. As a result the force of attraction of the nucleus for the valence electrons further decreases and hence the ionization enthalpy decreases.

$$\frac{1}{2} Br_2 + e^- \longrightarrow Br^- + 3.36 \text{ eV}$$

Energy released from 80 g gaseous bromine $= 3.36 \times 23.06$ kcal

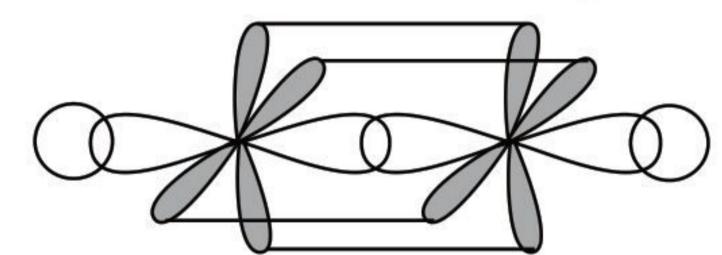
- :. Energy released for conversion of 8g gaseous bromine into Br ions $\frac{3.36 \times 23.06 \times 8}{80} = 7.748$ kcal
- 28. SF₆ molecule has octahedral geometry.

Formation of SF₆ (sp^3d^2 hydridisation): In SF₆ the central sulphur atom has the ground state outer electronic configuration $3s^23p^4$. In the exited state the available six orbitals *i.e.*, one s, three p and two d are singly occupied by electrons. These orbitals hybridise to form six new sp^3d^2 hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF₆. These six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds. Thus SF₆ molecule has a regular octahedral geometry.



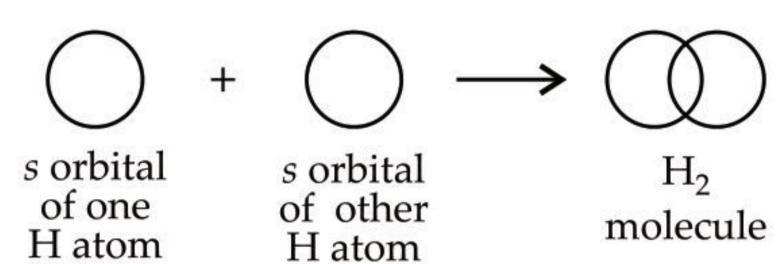
- 29. (a) Since the covalent bond depends on the overlapping of orbitals between different orbitals, the geometry of the molecule is different. The orientation of overlap is the factor responsible for their directional nature.
- (b) Due to presence of two lone pairs of electrons on oxygen atom in H_2O the repulsion between lp-lp is more. CO_2 undergoes sp hybridisation resulting in linear shape (O=C=O) while H_2O undergoes sp^3 hybridisation resulting in distorted tetrahedral or bent structure.
- (c) In ethyne molecule carbon undergoes *sp* hybridisation with two unhybridised orbitals. One *sp* hybrid orbital of one carbon atom overlaps axially with

sp hybrid orbital of the other carbon atom to form C—C sigma bond while



the other hybridised orbital of each carbon atom overlaps axially with s orbitals of hydrogen atoms forming σ bonds. Unhybridised orbitals form π bonds.

- **30.** (i) The oxidation state of Al is +3 and the covalency is 6.
- (ii) Electron gain enthalpy generally becomes more negative across a period as we move from left to right. However, adding an electron to the 2*p*-orbital leads to greater repulsion than adding an electron to the larger 3*p*-orbital. Hence, the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorus.
- 31. The main points of valence bond theory are
- (i) Only half filled orbitals are involved in overlapping.
- (ii) Atomic orbitals which are overlapping must have electrons with opposite spins.
- (iii) Strength of the bond depends upon extent of overlapping.
- (iv) Two atoms participating in bonding should come close to overcome the forces of repulsion. e.g., the optimum distance between the two atoms of hydrogen is balanced by forces of attraction and the energy of the system becomes minimum and is known as bond length.



(i) (a) According to Fajan's rule, higher the degree of ionic polarisation, greater is the covalent character.

Covalent character ∞ size of anion $\infty \frac{1}{\text{size of cation}} \infty$ charge on anion and cation

Hence, ionic character of ClF₃ will be less than that of LiF.

(b) M.O. electronic configuration of O_2 : $KK\sigma 2s^2\sigma^* 2s^2\sigma 2p_z^2\pi 2p_x^2 = \pi 2p_y^2\pi^* 2p_x^1 = \pi^* 2p_y^1$

Bond order =
$$\frac{8-4}{2}$$
 = 2

M.O. electronic configuration of F_2 :

$$KK\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^2 = \pi^* 2p_y^2$$

Bond order =
$$\frac{8-6}{2}$$
 = 1

Hence, O_2 has higher bond order than that of F_2 .

(c) Both the molecules NH_3 and NF_3 have pyramidal shape with a lone pair of electron on nitrogen atom. Although fluorine is more electronegative than nitrogen, the resultant dipole moment of NH_3 (4.90 × 10^{-30} C m) is greater than that of NF_3 (0.80 × 10^{-30} C m). This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N-H bonds whereas in NF_3 the orbital dipole is in the direction opposite to the resultant dipole moment of the three N-F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N-F bond moment which results in low dipole moment of NF_3 .

(iii) N atom in NO_2^+ ion is *sp*-hybridised while in NO_2^- , it is sp^2 -hybridised.

$$O=N^{+}=O, \begin{bmatrix} N \\ O & O \end{bmatrix}$$

Hence, NO₂⁺ has higher bond angle.

32. (i) I < Br < F < Cl (ii) $Pb^{4+} < Pb^{2+} < Pb$

(iii)
$$I_2 < Br_2 < Cl_2 < F_2$$
 (iv) $SiO_2 < P_2O_5 < SO_3 < Cl_2O_7$

(v) C < N < F < O

OR

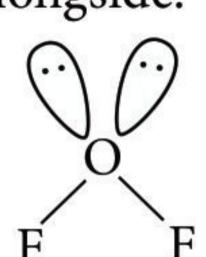
- (a) The name of element having ground state electronic configuration $3s^23p^5$ is chlorine (Cl).
- (b) The name of element having ground state electronic configuration $3s^23p^64s^2$ is calcium (Ca).
- (c) The name of element having ground state electronic configuration $3s^23p^63d^64s^2$ is iron (Fe).
- (d) The name of element having ground state electronic configuration $5s^25p^2$ is tin (Sn).

- (e) The name of element having ground state electronic configuration $5s^25p^6$ is xenon (Xe).
- **33.** (i) Only $SnCl_2$ has the same shape as $SO_2.SO_2$ and $SnCl_2$ both are AX_2L type molecule. Both have bent structure. While CO_2 and BeH_2 are AX_2 type with linear shape.

S'NO CI S'N CI

(ii) The Lewis structure of OF_2 is :F:O:F:, there are four pairs of electrons (two lone pairs and two bond pairs) around the central O atom. According to VSEPR theory, these electron pairs must be arranged tetrahedrally. Since the hybrid orbitals arranged tetrahedrally are obtained by sp^3 hybridisation, the oxygen atom involves sp^3 hybrid orbitals in bonding with fluorine. The structure of OF_2 is shown alongside.

The molecule of OF₂ is V-shaped with F—O—F bond angle of 103°18′. The normal tetrahedral angle of 109°28′ is decreased because of the strong repulsion of bond pairs by the two lone pairs of electrons.



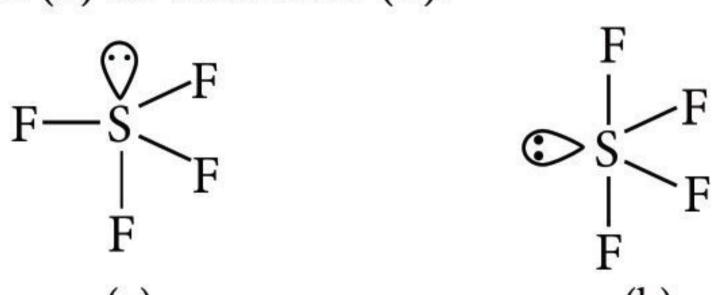
The oxidation number of F is always – 1. Hence, in OF_2 oxidation number of F = -1 oxidation number of O = +2

OR

(i) The decreasing order of repulsion is : lone pair-lone pair (lp-lp) > lone pair-bond pair (lp-bp)

> bond pair-bond pair (*bp-bp*)

- (ii) In ClF_3 , Cl, the central atom has five electron pairs (three are bond pairs and two are lone pairs). It is a AX_3L_2 type molecule. NF_3 is AX_3L type molecule and has a trigonal pyramidal shape.
- (iii) In SF_4 , the central S atom has five electron pairs (four bond pairs and one lone pair) whose arrangement should be trigonal bipyramidal. However, one of the electron pairs is lone pair. SF_4 can, therefore, have structure (a) or structure (b).



l.p. in the axial position l.p. in the equatorial position

In structure (a), there are three lp-bp repulsions at 90°. In structure (b), there are only two lp-bp repulsions at 90°. Hence, structure (b) is favoured one. The structure (b) is known as see-saw shape.



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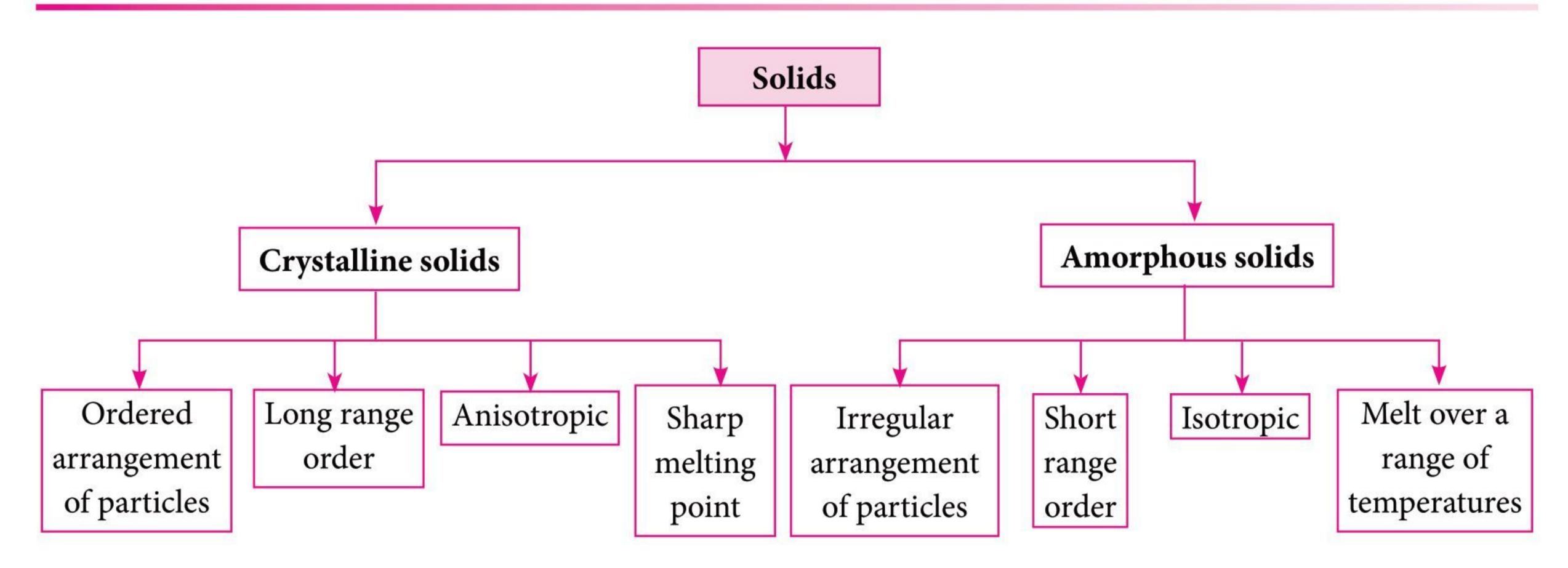


Solid State | Solutions

Solid State

Solids have high density and low compressibility as compared to gaseous as well as liquid phase.

CLASSIFICATION OF SOLIDS



Amorphous Solids

When constituent particles of a substance are not arranged in any regular arrangement, then the substance is said to be **amorphous**. Amorphous means no shape (Greek word "omorphe").

Crystalline Solids

The substances whose constituent particles are arranged in a definite geometric pattern in three-dimensional space are called **crystalline solids**.

Polycrystalline Solids

Besides crystalline and amorphous solids, there are some solids which apparently appear amorphous but have microcrystalline structures. These are called **polycrystalline solids**.

Types of Crystalline Solids and Their Properties

Type of Solid	Nature of Constituent Particles	Nature of Interaction between Particles	Physical and Electrical Properties	Examples
Molecular: (a) Non-polar (b) Polar (c) Hydrogen bonded	Molecules	(a) Dispersion or London forces(b) Dipole-dipole force(c) Hydrogen bonding	(a) Soft(b) Low melting points(c) Non-Conductors of electricity in both solid and liquid states	(a) H ₂ , CO ₂ (b) HCl, SO ₂ (c) H ₂ O
Ionic	Ions	Ionic (Coulombic or electrostatic) bonding	(a) Relatively hard(b) Brittle(c) High melting points(d) Non-conductors of electricity as solids, but conduct when melted	NaCl, MgO, ZnS
Metallic	Positive metal ions in a sea of delocalized free electrons	Metallic bonding	 (a) Range from very hard to very soft (b) Melting points range from high to low (c) Conduct electricity in both solid and liquid states (d) Have characteristic luster 	Fe, Mg, Cu
Network	Atoms and chemical subunits	Covalent bonding	 (a) Very hard (b) Very high melting points (c) Non-conductors of electricity (graphite is an exception) 	C(diamond) SiO ₂ (quartz) C(graphite)

STUDY OF CRYSTALS

- Crystal: A crystal is a homogenous portion of a solid substance made by regular pattern of structural units bounded by plane surface making definite angles with each other.
- Space lattice: The arrangement of constituent particles like atoms, ions or molecules in different sites in three dimensional space is called space lattice.
- Unit cell: The smallest repeating unit in space lattice which when repeats over and over again, results in a crystal of the given substance, is called unit cell.

- Face: Each crystal is made up of a definite geometric shape bounded by plane surfaces, called face.
- Edge: An edge is formed by the intersection of two adjacent faces.
- Interfacial angles: The angle between the two intersecting faces is called an interfacial angle.
 - A unit cell is described with the following parameters:
 - (a) The distances *a*, *b* and *c i.e.*, the length of the edges of unit cell.
 - (b) The angles α , β and γ between the three imaginary axes.

Types of unit cells (Primitive and Centred Unit Cell)

Primitive Unit Cell/ Simple Cubic Unit Cell

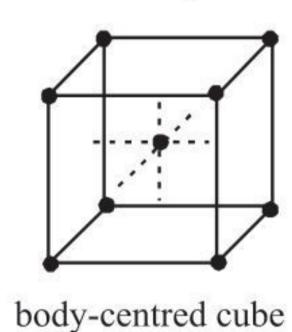
• Points are present only at the corners of the cell.

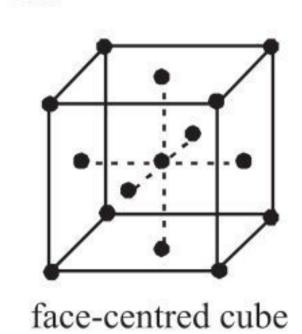
Centred unit cell

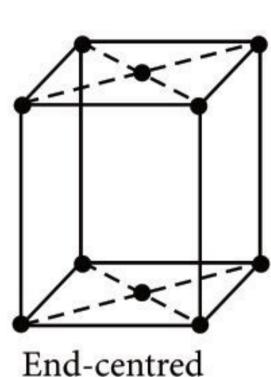
- When a unit cell contains one or more atoms ions or molecules present at position other than corners in addition to those at corner is called centred unit cell.
- **Body centred cubic unit cell** Points are present at the corners and an additional point is present at the body centre of the unit cell.
- Face centred cubic unit cell Points are present at the corners as well as centres of each of the six faces.
- End-centred: Points are present at the corners and at the centre of any two opposite faces.



simple cubic







= 52.4%

For simple cubic, number of atoms in a unit cell = 1 For bcc, number of atoms in a unit cell = 2 For fcc, number of atoms in a unit cell = 4 For end centred cubic, number of atoms in a unit cell = 2

Bravais Lattice

The crystal lattices of the substances may be categorised into seven types: Cubic, Tetragonal, Ortho-rhombic, Rhombohedral (trigonal), Hexagonal Monoclinic and Triclinic. These are called Bravais lattice.

PACKING FRACTION OR PACKING EFFICIENCY IN SOLIDS

• Packing fraction (density of packing) = v/Vwhere v = volume of the spherical atom = $\frac{4}{3}\pi r^3$ V = volume of the cube = a^3 For simple cubic, $r = \frac{a}{2}$; packing fraction = $\frac{\pi}{6}$ = 0.524

For *bcc*,
$$r = \frac{\sqrt{3}a}{4}$$
; packing fraction $= \frac{\sqrt{3}\pi}{8} = 0.68$
= 68%

For fcc,
$$r = \frac{a}{2\sqrt{2}}$$
; packing fraction = $\frac{\sqrt{2}\pi}{6} = 0.74$
= 74%

• For simple cubic, d = a;

For
$$bcc$$
, $d = \frac{\sqrt{3}a}{2}$; For fcc , $d = \frac{a}{\sqrt{2}}$

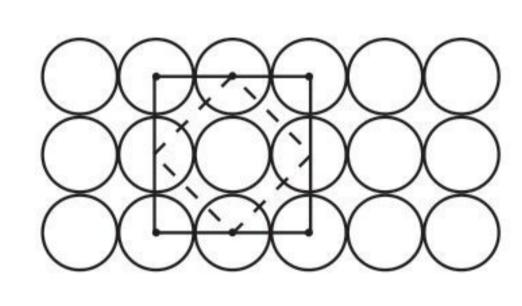
where *d* is the distance of nearest neighbours and *a* is the edge length of cubic unit cell.

PACKING OF CONSTITUENTS IN CRYSTALS (TWO-DIMENSIONS AND THREE-DIMENSIONS)

Constituents of a crystal have a tendency to pack as closely as possible to have maximum density and stability.

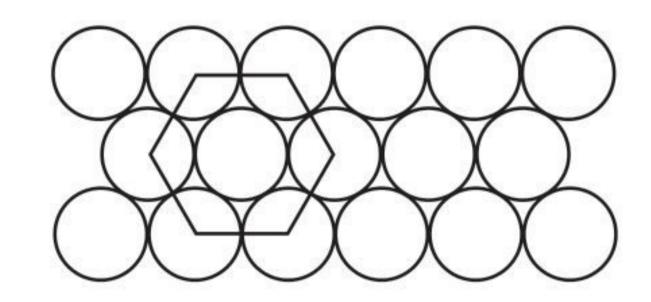
Square close packing

• This system has spheres of adjacent rows one over the other, showing a vertical as well as horizontal alignment to form a square.



Hexagonal close packing

• This system has spheres of every second row placed in the depression between spheres

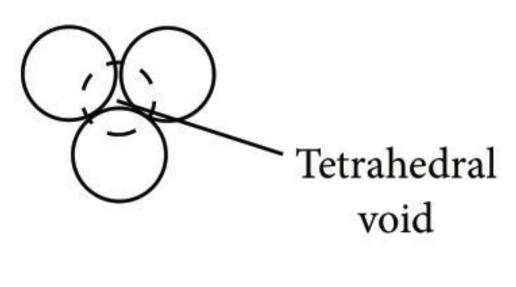


- of the first row. Subsequently, spheres of third row are vertically aligned with those of the first row. When this arrangement is continued indefinitely, the system obtained is found to possess hexagonal symmetry and is called hexagonal close packing of sphere and is abbreviated as *hcp* or *ABABAB*......
- **Body centred cubic :** This arrangement (*bcc*) is not the closest system, it is obtained when the spheres of the first row (layer) are slightly open and not in contact with each other.

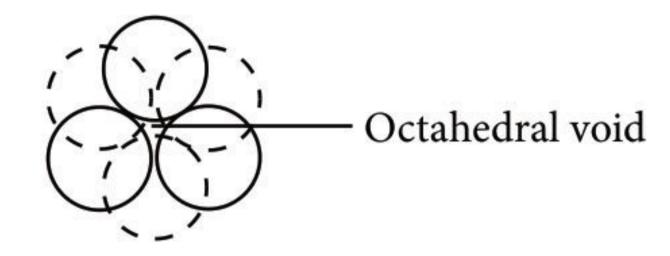
Void Space or Intersitial Sites

In a unit cell, some-empty space exists between spheres, this is called void space or hole, also called interstitial sites, or interstices.

Tetrahedral voids: These are holes or interstices surrounded by four spheres present at the corners of a tetrahedron. CN of tetrahedral void is 4.



Octahedral voids: There are holes surrounded by Radius ratio = $\frac{r}{}$ = $\frac{Radius}{}$ six spheres located on a regular octahedron. CN of octahedral void is 6.



Let the number of close packed spheres be *N*, then The number of octahedral voids = NThe number of tetrahedral voids = 2NTotal number of voids = 3N

COORDINATION NUMBER

The number of equidistant neighbour atoms that an atom has in its crystal structure. In case of ionic crystal, coordination number is equal to the number of oppositely charge ions surrounding a particular ion.

- simple cubic structure (scc) has CN = 6
- face centred cubic structure (fcc) has CN = 12
- body centred cubic structure (bcc) has CN = 8

Radius Ratio Effect and Shape of Crystals

The ratio of the radius of the cation to the anion in crystal lattice is called radius ratio.

Radius ratio =
$$\frac{r^+}{r^-}$$
 = $\frac{\text{Radius of the cation}}{\text{Radius of the anion}}$

Table shows the relationship of radius ratio, coordination number and the geometrical shapes of some ionic crystals.

Radius Ratio Rule

Limiting radius ratio $(r^+)/(r^-)$	CN	Shape
< 0.155	2	Linear
0.155-0.225	3	Trigonal planar
0.225-0.414	4	Tetrahedral
0.414 - 0.732	6	Octahedral
0.732-0.999	8	Body-centred cubic (bcc)
1	12	ccp and hcp

Crystal Structure of Some Cubic Ionic Solids

S.No.	Crystal Structure Units	Brief description and examples	Co-ordination Number	No. of formula per unit cell
(i)	Rock Salt	Cl ⁻ ions form <i>ccp</i> , Na ⁺ ions occupy all the	$Na^+ - 6$	4
	(NaCl-type)	octahedral voids. Examples: Halides of Li,	Cl ⁻ - 6	
		Na, K and Rb, AgCl, AgBr, NH ₄ Cl etc.		
(ii)	CsCl-type	Cl^- ions at the corners of cube, form bcc	$Cs^+ - 8$	1
		structure. Cs ⁺ ions occupy the cubic void.	Cl ⁻ - 8	
		Examples: CsCl, CsBr, CsI etc.		
(iii)	Zinc blende	S^{2-} ions form ccp , Zn^{2+} ions occupy alternate	$Zn^{2+}-4$	4
	(ZnS)	tetradedral voids.	$S^{2-} - 4$	
		Examples: ZnS, CuCl, CuBr, CuI, AgI etc.		
(iv)	Fluorite	Ca ²⁺ ions (+ve ions) form <i>ccp</i> and F ⁻ ions	$Ca^{2+} - 8$	4
	structure	(-ve ions) present in all the tetrahedral	F^4	
	(CaF ₂ – type)	voids. Examples: CaF ₂ , SrF ₂ , BaF ₂ , BaCl ₂		
		etc.		
(v)	Antifluorite	Negative ions <i>i.e.</i> , O^{2-} form <i>ccp</i> and positive	Li ⁺ – 4	4
	structure	Li ⁺ ions present in all the tetrahedral voids.	$O^{2-} - 8$	
	(Li ₂ O – type)	Example: Na ₂ O		

- (a) Effect of pressure on crystal structure: Increase of pressure increases the co-ordination number during crystallization *e.g.*, by applying high pressure, the NaCl crystal structure having 6: 6 co-ordination number changes to CsCl crystal structure having co-ordination number 8:8.
- (b) Effect of temperature on crystal structure: Increase of temperature decreases the coordination number *e.g.*, upon heating to 760 K, the CsCl crystal structure having co-ordination of 8 : 8 changes to NaCl crystal structure having co-ordination of 6 : 6.

NaCl type crystal $\leftarrow \frac{\text{high pressure}}{\text{heat, 760 K}}$ CsCl type crystal (8:8 co-ordination)

DENSITY OF UNIT CELL

$$d = \frac{Z \times M}{N_A \times a^3}$$

Z = Number of atoms in unit cell

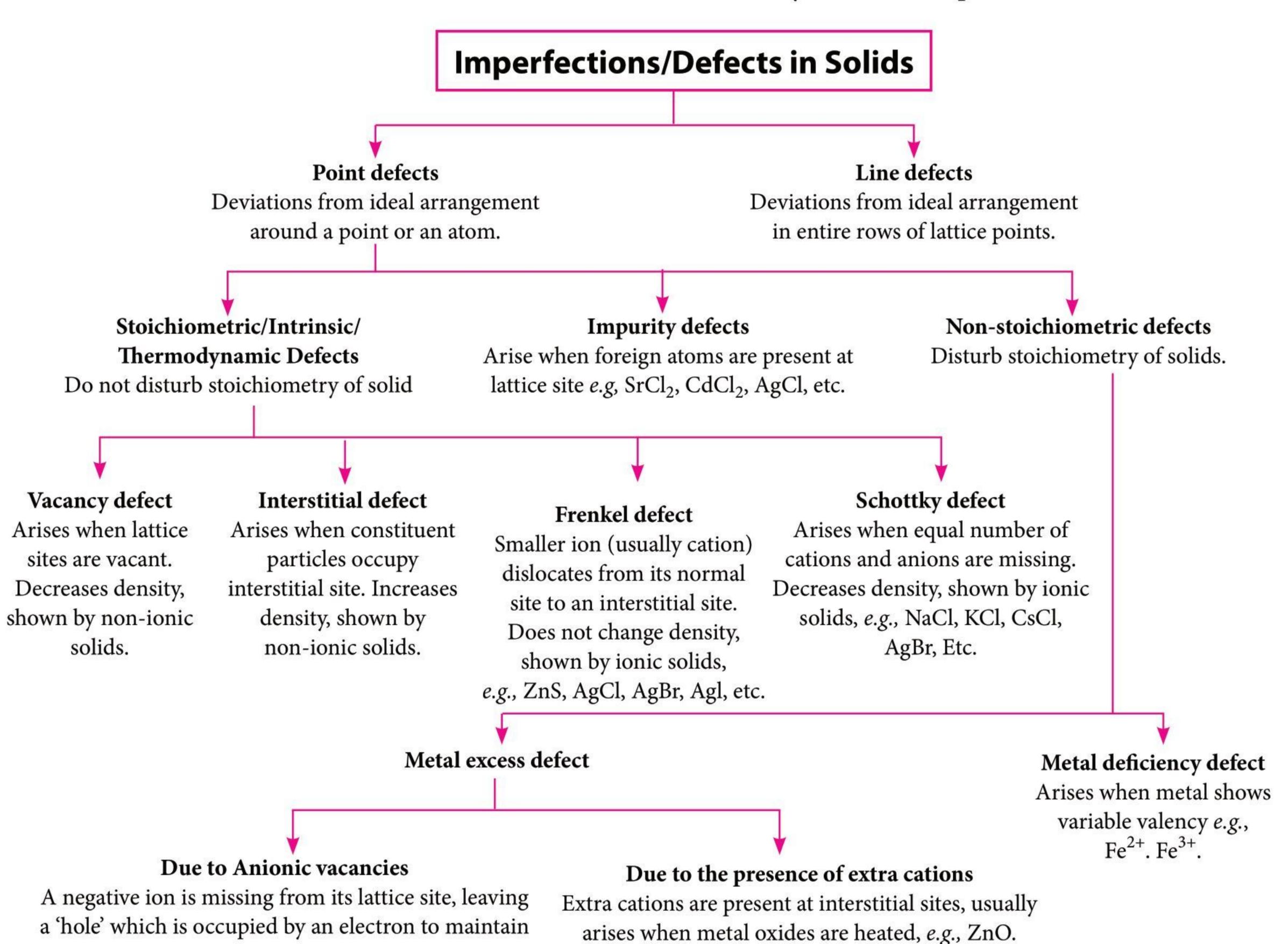
M = Mass of atom/sphere/element

 N_A = Avogadro number

a = Edge length

CRYSTAL DEFECT OR IMPERFECTIONS IN SOLIDS

In a crystalline solid, the atoms, ions or molecules are arranged in a definite repeating pattern, but some defects may occur in the pattern.



ELECTRICAL PROPERTIES OF SOLIDS

Solids may be classified into three categories depending upon the values of their electrical conductivity.

electrical neutrality, e.g., LiCl, NaCl. This defect product

F-centres.

Conductors

Solids which allow passage of maximum portion of electric current through themselves are called conductors. The electrical conductivity of these solids is of the order of 10⁴ to 10⁷ ohm⁻¹ m⁻¹.

Insulators

Solids which do not practically allow the electric current to pass through them are called insulators. The electrical conductivity is of the order of 10^{-20} to 10^{-10} ohm⁻¹ m⁻¹.

Semiconductors

Semiconductors are the solids whose electrical conductivity at normal temperature lies between that of a good conductor and an insulator. Electrical conductivity is of the order of 10^{-6} to 10^4 ohm⁻¹ m⁻¹. Semiconductors are of two types:

- (a) Intrinsic semiconductors: The semiconductors which show electrical conductivity because of internal disorders without adding external substances are called intrinsic semiconductors.
- **(b)** Extrinsic semiconductors: Semiconductors due to impurity defects.
- *n*-type semiconductors: Doping with electron rich impurities, *e.g.*, group 14 elements like Si or Ge with group 15 elements like P, As etc. Free electrons become available which increase conductivity. Such solids are called *n*-type semiconductors.
- *p*-type semiconductors: Doping with electron deficient impurities, *e.g.*, group 14 elements like Si or Ge with group 13 elements like B, Al or Ga. As a result, holes are created. Electrons move to occupy the holes. Thus, holes move towards negatively

charged plate as if they carry positive charge. These are called *p*-type semiconductors.

Magnetic Properties of Solids

Solid substances can be divided into different classes:

- **Diamagnetic substances:** These are weakly repelled by magnetic field. They have all the electrons paired, *e.g.*, NaCl, Benzene.
- Paramagnetic substances: They have magnetic dipoles due to the presence of unpaired electrons and thus are attracted by magnetic field, e.g., TiO, VO₂, Cu²⁺, Fe³⁺ but they lose their magnetism in the absence of a magnetic field.
- Ferromagnetic substances: These substances show permanent magnetism like Fe and CrO₂. A spontaneous alignment of magnetic moments in the same direction give rise to ferromagnetism.
- Anti-ferromagnetism: Some substance have domain structure similar to ferromagnetic substance but their domain are oppositely oriented and cancel out each other, then magnetic moment is zero, *e.g.*, MnO, MnO₂ etc.
- Ferrimagnetic: They have unequal number of parallel and antiparallel domains and have some net magnetic moment. They are weakly attracted by magnetic field as compared to ferromagnetic e.g., Fe₃O₄, ZnFe₂O₄ etc.



Introduction

Solution: When two or more chemically non-reacting substances are mixed to form a homogeneous mixture, it is called solution.

- (i) **Solute:** The component present in lesser amount is called solute.
- (ii) **Solvent:** The component present in greater amount is called the solvent.
- (iii) When the solution is composed of only two chemical substances, it is termed as binary solution. Similarly, it is called ternary and quaternary, if it is composed of three and four components respectively.

PROPERTIES OF A SOLUTION

(i) A solution consists of a single phase. *i.e.*. it is a monophasic system.

- (ii) A solution is uniform throughout. So it has uniform properties such as density, refractive index etc.
- (iii) The components of a solution can not be easily separated by physical methods.
- (iv) Size of solute particles in a solution is less than 1 nm in diameter.
- (v) The properties of a solution are the properties of its components, *i.e.*, the components do not lose their properties when they form a solution.
- (vi) Certain properties of solution such as density, viscosity, surface tension, boiling point, freezing point, etc. vary with the composition of the solution.

CONCENTRATION AND METHODS FOR EXPRESSING CONCENTRATION OF A SOLUTION

• The amount of solute present in the given quantity of the solution is known as the **concentration** of the solution.

Mass % =
$$\frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$$

Volume % =
$$\frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$$

Parts Per Million or ppm

• It is defined as the parts of a component per million parts of the solution.

ppm of
$$A = \frac{\text{Mass of component } A}{\text{Total mass of solution}} \times 10^6$$

Molarity

• It is defined as the number of moles of the solute dissolved per litre of the solution.

Molarity
$$(M) = \frac{n}{V} \times 1000 = \frac{w}{M_{w} \times V} \times 1000$$

For dilution, $M_1V_1 = M_2V_2$

For a mixture, $M_1V_1 + M_2V_2 + ... = M_R(V_1 + V_2 + ...)$

- Units of molarity: $mol L^{-1}$ and $mol dm^{-3}$.
- Molarity changes with temperature because of expansion or contraction of the volume of the liquid with temperature.

Molality

• It is defined as the number of moles of solute dissolved per 1000 g or per kg of the solvent.

Molality
$$(m) = \frac{n}{W} \times 1000 = \frac{w}{M_w \times W} \times 1000$$

- Units of molality: $mol kg^{-1}$.
- Molality is considered better for expressing the concentration as compared to molarity because molality does not change with temperature since mass of the solvent does not change with change in temperature.

Mole Fraction

• It is defined as the ratio of the number of moles of one component to the total number of moles present in the solution.

Mole fraction of
$$A(x_A) = \frac{n_A}{n_A + n_B}$$

$$x_A + x_B = 1 \Longrightarrow x_A = 1 - x_B \text{ or } x_B = 1 - x_A$$

Mole fraction is independent of temperature.

Normality

• It is defined as the number of gram equivalents of the solute dissolved per litre of the solution.

- Normality $(N) = \frac{w}{E \times V} \times 1000$
- Units of normality: g equiv. L⁻¹
- Normality of a solution also changes with temperature.
- Normality = $n \times$ Molarity
- For acids, Normality = Molarity × Basicity
- For bases, Normality = Molarity × Acidity

Formality

 It is defined as the number of formula masses of the solute dissolved per litre of the solution.

Formality =
$$\frac{\text{No. of formula mass of solute}}{\text{Vol. of solution (L)}}$$

SOLUBILITY

Solubility of a substance is the maximum amount of it that can be dissolved in a specified amount of a solvent to form a saturated solution at a given temperature.

Steps of Solution Formation

- Step-1: Breaking up the solute into individual components (expanding the solute): Endothermic.
- Step-2 : Overcoming intermolecular forces in the solvent to make room for the solute (expanding the solvent) : Endothermic.
- Step-3 : Allowing the solute and solvent to interact to form the solution : Often exothermic.

Enthalpy (Heat) of Solution

- $\Delta H_{\text{soln}} = \Delta H_{\text{step 1}} + \Delta H_{\text{step 2}} + \Delta H_{\text{step 3}}$
- $\Delta H_{\rm soln}$ may have positive or a negative sign. Enthalpy of hydration ($\Delta H_{\rm hyd}$) includes ΔH of step 2 and 3.
- Factors favouring the solution process
 - Negative value for ΔH_{soln}
 - Increase in entropy
 - For positive value of ΔS_{soln} , it is the increase in entropy that outweighs the increase in energy and causes the solution process to occur.

Henry's Law:

- Henry's law states that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution" and is expressed as $p = K_H x$
 - Here K_H is the Henry's law constant.

Effect of Pressure

 Henry's law works best for dilute solutions of gases that do not dissociate or react with the solvent. • Liquids and solids exhibit practically no change of solubility with changes in pressure.

Effect of Temperature

- Increase in temperature usually increases solubility of solids.
- Solubility of gases always decreases with increasing temperature.

VAPOUR PRESSURE OF SOLUTIONS

- Vapour pressure of a liquid/solution is the pressure exerted by the vapours in equilibrium with the liquid solution at a particular temperature.
- Liquids which have weak intermolecular forces are more volatile and have a higher vapour pressure.

Raoult's law

It states that in a solution, the partial pressure of a component at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state. For a solution containing components *A* and *B*,

$$p_A = x_A \times p_A^0 \text{ and } p_B = x_B \times p_B^0$$

 $\therefore P_{\text{total}} = p_A + p_B = x_A p_A^0 + x_B p_B^0 = (1 - x_B) p_A^0 + x_B p_B^0$
or, $P_{\text{total}} = (p_B^0 - p_A^0) x_B + p_A^0$
We know, $x_A + x_B = 1$

Substituting number of moles,

$$P_{\text{total}} = p_A^0 \frac{n_A}{n_A + n_B} + p_B^0 \frac{n_B}{n_A + n_B}$$

or, substituting weights and molecular weights,

$$P_{\text{total}} = p_A^0 \frac{w_A / M_A}{\frac{w_A}{M_A} + \frac{w_B}{M_B}} + p_B^0 \frac{w_B / M_B}{\frac{w_A}{M_A} + \frac{w_B}{M_B}}$$

Raoult's law is valid only for ideal solutions.

Ideal and Non-ideal Solutions

• **Ideal solution** is a solution in which the interactions between A and B are of the same magnitude as in the pure components, or is a solution which obeys Raoult's law at all temperatures and concentrations. For ideal solution; $\Delta V_{\text{mixing}} = 0$, $\Delta H_{\text{mixing}} = 0$

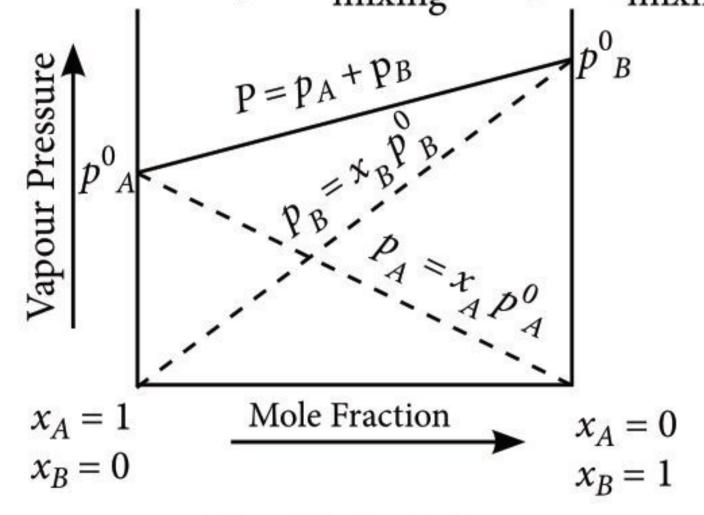


Fig.: Ideal solution

- **Non-ideal solution** is a solution in which A B interactions are of different magnitudes than those in pure components, or $\Delta V_{\text{mixing}} \neq 0$ and $\Delta H_{\text{mixing}} \neq 0$. These solutions do not obey Raoult's law.
- Non-ideal solutions showing positive deviation: In this case, the total vapour pressure determined experimentally is higher than that calculated from Raoult's law. This is due to weaker (lower) interactions than in pure components, *e.g.* ethanol and cyclohexane, the inter-molecular H-bonding in ethanol is reduced on adding cyclohexane. Solution showing +ve deviation boils at a lower temperature than expected, also ΔV_{mixing} = +ve and ΔH_{mixing} = +ve.

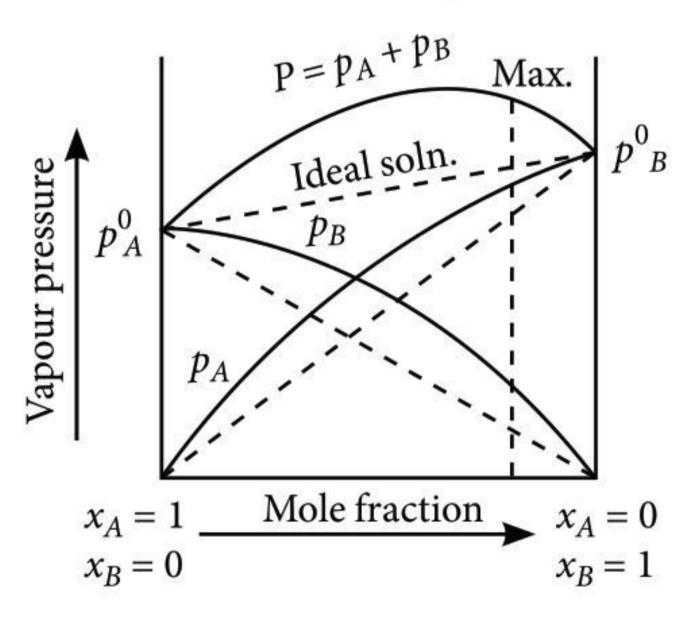


Fig.: Non-ideal solution showing positive deviation

• Non-ideal solutions showing negative deviation: In this case, the total vapour pressure determined experimentally is lower than that calculated from Raoult's law. This is due to stronger interactions than in pure components, *e.g.*, chloroform and acetone, show –ve deviation due to new H-bonding between chloroform and acetone molecules.

Solution showing –ve deviation boils at a relatively higher temperature than expected, also

$$\Delta V_{\text{mixing}} = -\text{ve}$$
 and $\Delta H_{\text{mixing}} = -\text{ve}$.

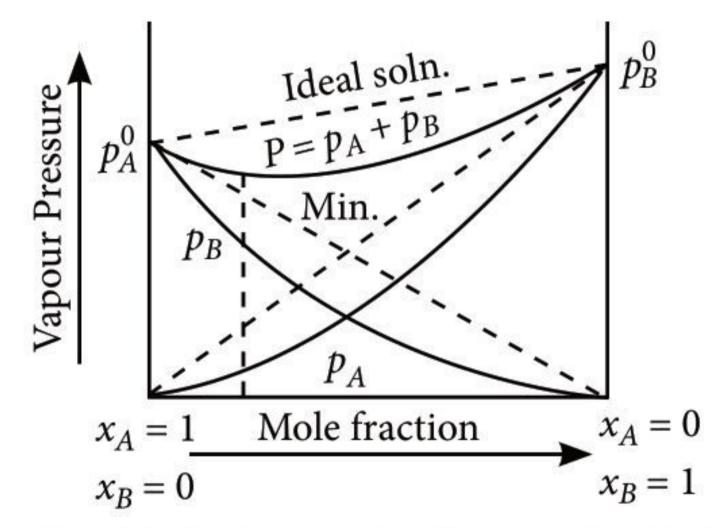


Fig.: Non-ideal solution showing negative deviation

 Azeotropes: The mixtures of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as vapour phase are called **constant boiling mixtures** or **azeotropic mixtures**.

- Minimum boiling azeotropes: These are formed by those liquid pairs which show large positive deviations from ideal behaviour, e.g., ethanol-water mixture.
- Maximum boiling azeotropes: These are formed by those liquid pairs which show large negative deviations from ideal behaviour, e.g., nitric acid-water mixture.

COLLIGATIVE PROPERTIES

They depend only on the number of species present in the solution and not on their nature.

• Relative lowering of vapour pressure: Relative lowering of vapour pressure is equal to mole fraction of the solute in a dilute solution.

$$\frac{P^{\circ} - P_{s}}{P^{\circ}} = x_{B} = 1 - x_{A} \qquad (\because x_{A} + x_{B} = 1)$$
or
$$\frac{\Delta P}{P^{\circ}} = x_{B} = \frac{n_{B}}{n_{A} + n_{B}}$$

• Elevation in boiling point (Ebullioscopy): The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure. Boiling point of a solvent is elevated by the addition of non-volatile solute.

i.e., Elevation in boiling point (ΔT_b)

= Boiling point of solution – Boiling point of pure solvent

$$\Delta T_b = K_b m = K_b \times \frac{W_B \times 1000}{m_B \times W_A}$$

where K_b = molal elevation constant, m = molality

- For every mole of particles dissolved in a litre of water, the boiling point of water increases by about 0.5 °C like for adding 1 mole sucrose in 1 litre water will increase b.pt. of water from 100 to 100.5 °C while adding 1 mole of NaCl (2 particles) increases the b.pt. from 100 °C to 101 °C.
- Depression in freezing point (Cryoscopy):

 Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid.

Depression in freezing point (ΔT_f)

= Freezing point of the solvent – Freezing point of the solution

$$\Delta T_f = K_f m$$

$$\Delta T_f = K_f \times \frac{W_B \times 1000}{m_B \times W_A}$$

where K_f = molal depression constant, m = molality

- For every mole of particle in a litre of water, the freezing point decreases by about 1.9 °C.
- Osmotic pressure (π) : It is the pressure necessary to just stop the flow of solvent across a semipermeable membrane.

$$\pi = CRT \text{ or } \pi = \left(\frac{n_2}{V}\right)RT$$

where, R = gas constant, C = molarity of the solution T = given temperature, $n_2 = \text{number of moles of solute}$ V = volume of solution (in L)

- Berkely-Hartley method is used to determine osmotic pressure.
 - Solutions having the same osmotic pressure
 → Isotonic solutions.
 - Solutions of low osmotic pressure →
 Hypotonic solutions.
 - Solutions of high osmotic pressure →
 Hypertonic solutions.

ABNORMAL MOLAR MASS

As colligative properties $\propto \frac{1}{(\text{molar mass})}$

 $\therefore \frac{\text{Abnormal colligative property}}{\text{Normal colligative property}} = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$

Van't Hoff Factor (i)

It is defined as the ratio of the normal mass to the observed molar mass of the solute *i.e.*,

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

Since, molar mass
$$\propto \frac{1}{\text{Colligative property}}$$

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

= Total number of particles after association/dissociation
No. of particles before association/dissociation

The value of *i* depends upon the state of solute in the solution. Following cases become possible:

- (a) When i = 1, then the solute remains unaffected (i.e., normal) in solution.
- (b) When i > 1, then the solute undergoes dissociation in solution.
- (c) When, i < 1, then the solute undergoes association in solution.

(i) Van't Hoff Factor and Degree of **Association**

Degree of association, $\alpha = \frac{i-1}{1} = (1-i)\frac{n}{n-1}$

(ii) Van't Hoff Factor and Degree of Dissociation

Degree of dissociation, $\alpha = \frac{i-1}{n-1}$

Colligative Properties in Terms of Van't Hoff Factor (i)

- Relative lowering of vapour pressure $\frac{P_A^0 P_S}{P^0} = ix$
- Elevation in boiling point : $\Delta T_b = iK_b \cdot m$
- Depression in freezing point : $\Delta T_f = iK_b \cdot m$
- Osmotic pressure : $\pi = iCRT$



MCQs TYPE QUESTIONS

- 1. Solids which do not show the same physical properties in different directions are called
 - (a) pseudo solids
 - (b) isotropic solids
 - (c) polymorphic solids
 - (d) anisotropic solids.
- 2. You have two different HCl solutions having concentration 3 M and 1 M respectively. How many mL of both solutions should be mixed to form 1 L of 1.2 M?
 - (a) 900 mL of 1 M and 100 mL of 3 M
 - (b) 100 mL of 1 M and 900 mL of 3 M
 - (c) 500 mL of each
 - (d) 333.33 mL of 3 M and 666.66 mL of 1 M
- Boiling point of benzene is 353.23 K. When 1.8 g of non-volatile solute is dissolved in 90 g of benzene. Then boiling point is raised to 354.11 K. Given K_b (benzene) = 2.53 K kg mol⁻¹. The molecular mass of non-volatile substance is

 - (a) 58 g mol^{-1} (b) 120 g mol^{-1}
 - (c) 116 g mol^{-1} (d) 60 g mol^{-1}
- Doping of silicon with P or Al increases the conductivity. The difference in the two cases is

- (a) P is non-metal whereas Al is a metal
- (b) P is a poor conductor while Al is a good conductor
- (c) P gives rise to extra electrons while Al gives rise to holes
- (d) P gives rise to holes while Al gives rise to extra electrons.
- 5. 1 M, 2.5 litre NaOH solution is mixed with another 0.5 M, 3 litre NaOH solution. Then find out the molarity of resulting solution.
 - (a) 0.80 M (b) 1.0 M (c) 0.73 M (d) 0.50 M
- Y g of non-volatile organic substance of molecular mass M is dissolved in 250 g benzene. Molal elevation constant of benzene is K_b . Elevation in its boiling point is given by

(a)
$$\frac{M}{K_b Y}$$
 (b) $\frac{4K_b Y}{M}$ (c) $\frac{K_b Y}{4M}$ (d) $\frac{K_b Y}{M}$

- 7. In a hexagonal close packed (hcp) structure of spheres, the fraction of the volume occupied by this sphere is A. In a cubic close packed structure this packing fraction is *B*. The relation for *A* and *B* is
 - (a) A = B
 - (b) A < B
 - (c) A > B
 - (d) A is equal to the fraction in a simple cubic lattice.

- 8. Which of the following plots represents the behaviour of an ideal binary solution?
 - (a) Plot of $1/P_{\text{total}}$ vs y_A (mole fraction of A in vapour phase) is linear.
 - (b) Plot of P_{total} vs y_{B} is linear.
 - (c) Plot of P_{total} vs y_A is linear.
 - (d) Plot of $1/P_{\text{total}}$ vs y_{B} is non-linear.
- 9. Electrolyte A gives three ions and B is a non-electrolyte. If 0.1 M solution of solute B produces an osmotic pressure of 2p, then 0.05 molar solution of A will produce an osmotic pressure equal to
 - (a) p
- (b) 1.5p (c) 2p
- (d) 3p
- 10. Which of the following is a ferromagnetic compound?

 - (a) C_6H_6 (b) Fe_3O_4 (c) CrO_2
- (d) NaCl
- 11. To aqueous solution of NaI, increasing amounts of solid HgI₂ is added. The vapour pressure of the solution
 - (a) decreases to a constant value
 - (b) increases to a constant value
 - (c) increases first and then decreases
 - (d) remains constant because HgI₂ is sparingly soluble in water.
- 12. If edge of a bcc crystal of an element is a cm, M is the atomic mass and N_0 is Avogadro number, then density of the crystal is
 - (a) $\frac{4M}{a^3N_0}$ (b) $\frac{2N_0}{Ma^3}$ (c) $\frac{2M}{N_0a^3}$ (d) $\frac{Ma^3}{2N_0}$

- 13. Assertion: In close packing of spheres, a tetrahedral void is surrounded by four spheres whereas an octahedral void is surrounded by six spheres.

Reason: A tetrahedral void has a tetrahedral shape whereas an octahedral void has an octahedral shape.

- (a) Both assertion and reason are true and reason is the correct explanation for assertion.
- (b) Both assertion and reason are true but reason is not the correct explanation for assertion.
- (c) Assertion is true but reason is false.
- (d) Both assertion and reason are false.
- **14.** A metal has *bcc* structure and the edge length of its unit cell is 3.04 Å. The volume of the unit cell in cm³ will be
 - (a) $1.6 \times 10^{-21} \text{ cm}^3$ (b) $2.81 \times 10^{-23} \text{ cm}^3$ (c) $6.02 \times 10^{-23} \text{ cm}^3$ (d) $6.6 \times 10^{-24} \text{ cm}^3$

15. Match the column I with column II and select the correct option.

	Column-I		Column-II
(1)	Raoult's law	(p)	$\Delta T_f = K_f.m$
(2)	Henry's law	(q)	$\pi = CRT$
(3)	Elevation in boiling point	(r)	$P = x_1 p_1^{\circ} + x_2 p_2^{\circ}$
(4)	Depression in freezing point	(s)	$\Delta T_b = K_b . m$
(5)	Osmotic Pressure	(t)	$P = K_H . x$

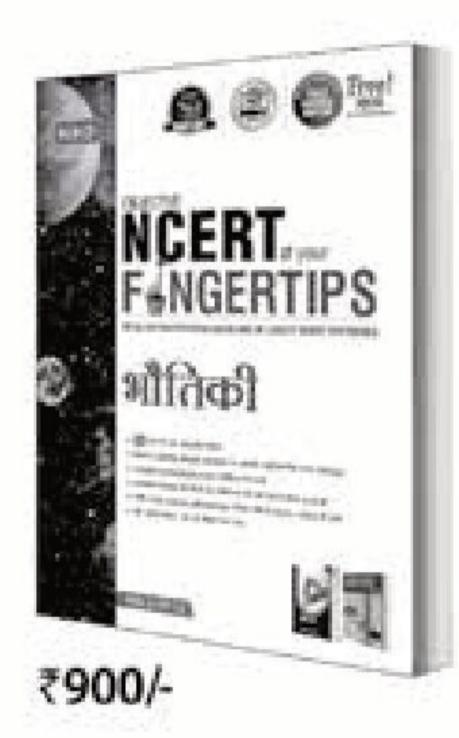
- (a) 1 (r), 2 (t), 3 (s), 4 (p), 5 (q)
- (b) 1 (t), 2 (r), 3 (q), 4 (s), 5 (p)
- (c) 1 (p), 2 (t), 3 (r), 4 (q), 5 (s)
- (d) 1 (s), 2 (p), 3 (q), 4 (r), 5 (t)
- 16. For an ideal binary liquid solution with $P_A^{\circ} > P_B^{\circ}$, in which relation between x_A (mole fraction of A in liquid phase) and y_A (mole fraction of A in vapour phase) is correct? x_B and y_B are mole fraction of B in liquid and vapour phase respectively.
 - (a) $x_A = y_A$
- (b) $x_A > y_A$
- (c) $\frac{x_A}{} < \frac{y_A}{}$ x_B y_B
- (d) x_A , y_A , x_B and y_B cannot be correlated
- 17. Total volume of atoms present in a face-centred cubic unit cell of a metal is (*r* is atomic radius)
 - (a) $\frac{12}{3}\pi r^3$
- (b) $\frac{16}{3}\pi r^3$
- (d) $\frac{24}{3}\pi r^3$
- **18.** Match the distribution of particles *A* and *B* in List I with formula given in List II and select the correct option.

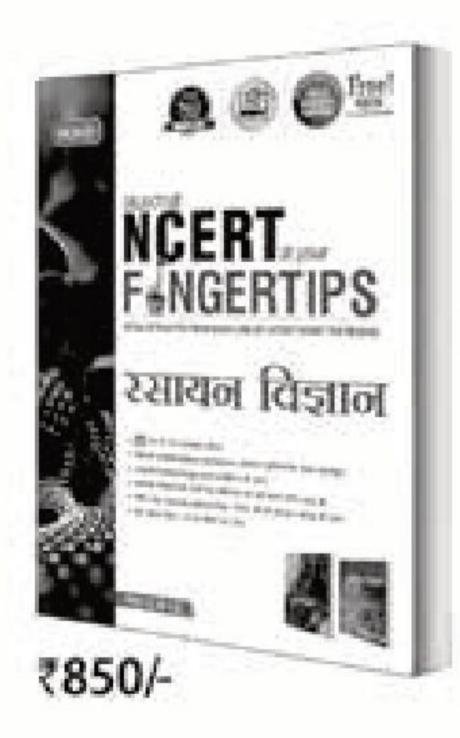
	List I		List II
P.	A in <i>ccp</i> and B equally distributed in octahedral and tetrahedral	1.	A_2B_3
Q.	<i>B</i> in <i>hcp</i> and <i>A</i> occupy 2/3rd of octahedral voids	2.	A_3B
R.	A at the corners and face centres and B at edge centres and body centre	3.	AB
S.	<i>B</i> in <i>ccp</i> and <i>A</i> occupy all the octahedral and tetrahedral sites	4.	AB_2

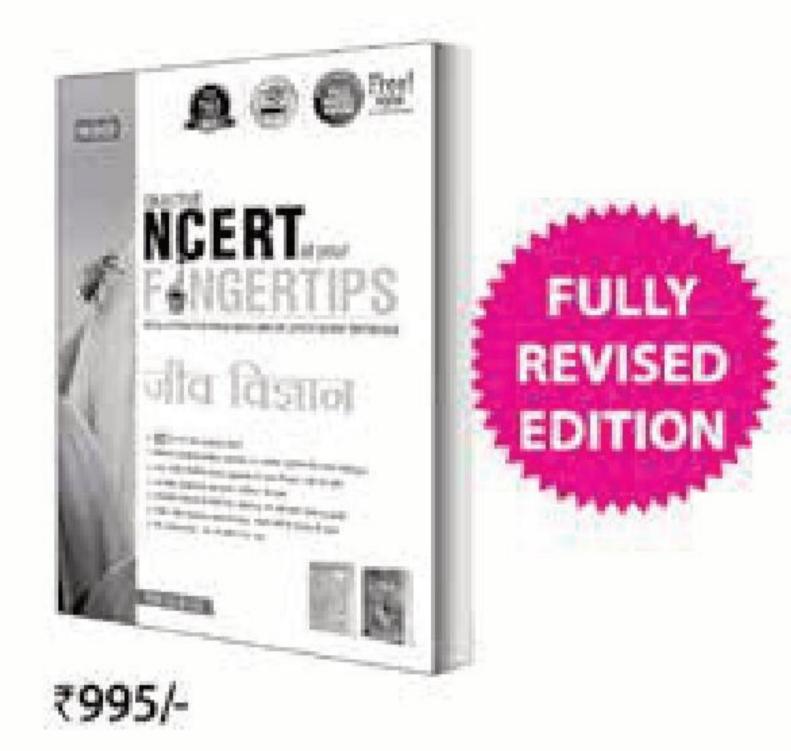
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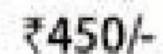
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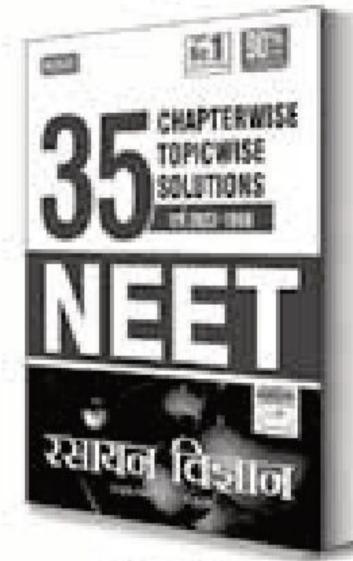
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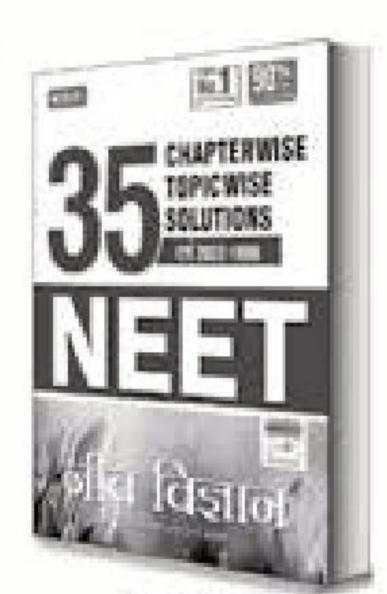
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- (a) 4 1 3 2 (b) 4 1 2 3 (c) 3 2 1 4 (d) 4 2 3 1
- 19. Which pair will not form an ideal solution?
 - (a) C_2H_5Br and C_2H_5Cl
 - (b) C_6H_5Br and C_6H_5I
 - (c) C₆H₆ and C₆H₅CH₃Cl
 - (d) C_2H_5I and C_2H_5OH
- 20. Assertion: 0.1 M glucose solution has higher depression in the freezing point than 0.1 M urea solution.

Reason : K_f for both has same values.

- (a) If both assertion and reason are correct and reason is the correct explanation of the assertion.
- (b) If both assertion and reason are correct but reason is not the correct explanation of the assertion.
- (c) If assertion is correct but reason is incorrect.
- (d) If assertion is incorrect but reason is correct.

NUMERICAL VALUE TYPE QUESTIONS

- 21. The value of P° for benzene is 640 mm of Hg. The vapour pressure of solution containing 2.5 g substance in 39 g benzene is 600 mm of Hg. The molecular mass of *X* is______.
- 22. Silver (Atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm⁻³. The number of silver atoms on a surface of area 10^{-12} m² can be expressed in scientific notation as $y \times 10^x$. The value of x is_____.
- 23. The freezing point of 0.1 M solution of glucose is -1.86 °C. If an equal volume of 0.3 M glucose solution is added, the freezing point (in °C) of the mixture will be .
- 24. The ratio of coordination number of each sphere in *ccp* and *hcp* in three dimension is_____.
- 25. If N₂ gas is bubbled through water at 293 K, how many millimoles of N₂ gas would dissolve in 1 litre of water? Assume that N₂ exerts a partial pressure of 0.987 bar. The K_H for N_2 at 293 K is 76.48 kbar.

SOLUTIONS

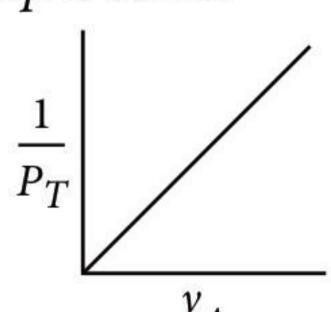
- 2. (a): Let x mL of 3 M and (1000 x) mL of 1 M HCl are mixed.

- $M_1V_1 + M_2V_2 = M_3V_3$ $3x + 1(1000 - x) = 1.2 \times 1000 \implies x = 100 \text{ mL}$ Thus, 100 mL of 3 M and 900 mL of 1 M HCl should be mixed.
- 3. (a): $T_b^{\circ} = 353.23 \text{ K}$, $W_B = 1.8 \text{ g}$, $W_A = 90 \text{ g}$, $T_b = 354.11 \text{ K}, K_b = 2.53 \text{ K kg mol}^{-1}$ $\Delta T_b = T_b - T_b^{\circ} = 354.11 - 353.23 = 0.88 \text{ K}$ $M_B = \frac{W_B \times K_b \times 1000}{\Delta T_b \times W_A} = \frac{1.8 \times 2.53 \times 1000}{0.88 \times 90}$ $= 57.5 \approx 58 \text{ g mol}^{-1}$
- (c): Doping of Si with P gives extra electrons (*n*-type) semiconductor while doping with Al give rise to holes (*p*-type) semiconductor.
- 5. (c): From molarity equation $M_1V_1 + M_2V_2 = M_3(V_1 + V_2)$ $1 \times 2.5 + 0.5 \times 3 = M_3 \times 5.5$ $M_3 = \frac{4}{5.5} = 0.727 \approx 0.73 \text{ M}$
- (b): Weight of solute = Yg; Molecular mass = $M \text{ g mol}^{-1}$ Weight of benzene (solvent) = 250 g

$$\Delta T_b = \frac{1000 \times K_b \times Y}{250 \times M} = \frac{4K_b Y}{M}$$

 \therefore plot of y_A vs $1/P_{\text{total}}$ is linear

- 7. (a): Packing efficiency of *hcp* and *ccp* is same.



- (d): For, electrolyte A, $\pi = icRT = 3 \times 0.05 RT$...(i) Osmotic pressure of B = 2p = 0.1 RT, p = 0.05 RT ...(ii) Since temperature is same, comparing equation (i) and (ii), we get osmotic pressure at A = 3p
- 10. (c)
- 11. (b): $2Na_{(aq)}^{+} + 2I_{(aq)}^{-} + HgI_{2(s)} \rightarrow 2Na_{(aq)}^{+} + HgI_{4(aq)}^{2-}$ The number of particles decreases from $5 = (2Na^{+} + 2I^{-} + HgI_{2})$ to $3 = (2Na^{+} + HgI_{4}^{2-})$.

MONTHLY TEST DRIVE CLASS XI ANSWER

- **2.** (a) (a)
- **7**. (c) **8.** (c) (b) **10**. (a) (c)
- **13**. (b) **11.** (c) **12.** (b) **15**. (b) **14**. (a)
- **18.** (b) **16.** (c) **17**. (a) **19.** (a) **20.** (a,c,d)
- **22.** (c,d) **23**. (a,d) **24.** (108.9)
- **25**. (0.246) **26.** (2091.32) **27**. (a)
- **29**. (c) **28**. (a) **30**. (b)

Hence, the colligative property will decrease or, the vapour pressure will increase to a constant value until NaI is completely consumed.

12. (c): Density of a crystal =
$$\frac{Z \times \text{Atomic mass}}{N_0 \times a^3}$$

For bcc, Z = 2, atomic mass = M

$$\therefore \text{ Density} = \frac{2 \times M}{N_0 a^3}$$

- 13. (b): Tetrahedral void is so called because it is surrounded by four spheres tetrahedrally, while octahedral void is so called because it is surrounded by six spheres octahedrally.
- 14. (b): Volume of unit cell = a^3 = $(3.04 \times 10^{-8} \text{ cm})^3 = 2.81 \times 10^{-23} \text{ cm}^3$
- 15. (a)
- **16.** (c): $P_A = P_A^{\circ} \cdot x_A = P_T \cdot y_A$, $P_B = P_B^{\circ} \cdot x_B = P_T \cdot y_B$

$$\therefore \frac{P_A^{\text{o}}}{P_B^{\text{o}}} \cdot \frac{x_A}{x_B} = \frac{y_A}{y_B} \quad \therefore \quad \frac{P_A^{\text{o}}}{P_B^{\text{o}}} > 1 \qquad \therefore \quad \frac{x_A}{x_B} < \frac{y_A}{y_B}$$

17. (b): The face centred cubic unit cell contains 4 atoms.

$$\therefore \text{ Total volume of atoms} = 4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3$$

- 18. (a) 19. (d)
- 20. (d): Depression in freezing point is a colligative property which depends on the number of particles and number of particles in both 0.1 M glucose and 0.1 M urea solutions will be same, hence depression in freezing points will be same.
- 21. (80): Relative lowering of vapour pressure

$$= \frac{P^{\circ} - P}{P^{\circ}} = \frac{n_2}{n_1 + n_2}; \frac{640 - 600}{640} = \frac{2.5 / M}{39 / 78}$$

$$M = \frac{640 \times 78 \times 2.5}{39 \times 40} = 80 \text{ g/mol}$$
 :: $n_2 <<<< n_1$

22. (7): Density =
$$\frac{\text{Mass}}{\text{Volume}}$$

 $10.5 \text{ g/cm}^3 \text{ means in } 1 \text{ cm}^3 \text{ Ag} = 10.5 \text{ g}$

No. of atoms in 1 cm³ =
$$\frac{10.5}{108} N_A$$

No. of atoms in 1 cm² =
$$\left(\frac{10.5}{108}N_A\right)^{2/3}$$

No. of atoms in 10^{-12} m² or 10^{-8} cm²

$$= \left(\frac{10.5}{108}N_A\right)^{2/3} \times 10^{-8}$$

$$= \left(\frac{10.5 \times 6.022 \times 10^{23}}{108}\right)^{2/3} \times 10^{-8} = 1.50 \times 10^{7}$$

$$x = 7$$

- 23. (3.72): $K_f = \Delta T_f/m = 1.86/0.1 = 18.6$ $M_1V_1 + M_2V_2 = M_3V_3$ $V_1 = V_2 = V$, $V_3 = (V + V) = 2V$ $0.1 \times V + 0.3 \ V = M_3 \times 2V \ \text{or} \ M_3 = 0.2$, $\Delta T_f = 18.6 \times 0.2 = 3.72 ^{\circ}\text{C} \implies T_f = -3.72 ^{\circ}\text{C}$
- 24. (1): Coordination number in ccp = 12Coordination in hcp = 12Ratio = 12/12 = 1
- 25. (0.716): The mole fraction of the gas in solution

$$x_{\text{N}_2} = \frac{P_{\text{N}_2}}{K_H} = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

If n is the number of moles of N_2 in solution and 1 litre of water contains 55.5 moles, then

$$x_{\text{N}_2} = \frac{n}{n+55.5} \approx \frac{n}{55.5} = 1.29 \times 10^{-5} \, (n << 55.5)$$

$$\therefore \quad n = 55.5 \times 1.29 \times 10^{-5} = 7.16 \times 10^{-4} \, \text{mol}$$

$$= 0.716 \, \text{mmol}$$



MtG

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Series-4

The d- and f-Block Elements

Time Allowed: 3 hours Maximum Marks: 70

GENERAL INSTRUCTIONS

General Instructions: Read the following instructions carefully.

- (a) There are 33 questions in this question paper. All questions are compulsory.
- (b) Section A : Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
- (c) Section B: Q. No. 17 to 25 are short answer questions and carry 2 marks each.
- (d) Section C: Q. No. 26 to 30 are short answer questions and carry 3 marks each.
- (e) Section D: Q. No. 31 to 33 are long answer questions carrying 5 marks each.
- (f) There is no overall choice. However, internal choices have been provided.
- (g) Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

Read the passage given below and answer the following questions:

1. The transition elements have incompletely filled *d*-subshells in their ground state or in any of their oxidation states. The transition elements occupy position in between s- and p-blocks in groups 3 to 12 of the periodic table. There are mainly three series of the transition metals, 3d series (Sc to Zn), 4d series (Y to Cd) and 5d series (La to Hg, omitting Ce to Lu). The fourth 6d series (Ac to Cn, omtting Th to Lr). In general, the electronic configuration of outer orbitals of these elements is $(n-1) d^{1-10} ns^{1-2}$. The very name 'transition' given to the elements of d-block is only because of their position between *s*-and *p*-block elements. All the transition elements have typical metallic properties such as high tensile strength, ductility, malleability. Except mercury, which is liquid at room temperature, other transition elements have typical metallic structures.

The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. Transition metals also form alloys. An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other.

The following questions are multiple choice questions. Choose the most appropriate answer.

- (i) Which of the following characteristics of transition metals is associated with higher catalytic activity?
 - (a) High enthalpy of atomisation
 - (b) Variable oxidation states
 - (c) Paramagnetic behaviour
 - (d) Colour of hydrated ions
- (ii) Transition elements form alloys easily because they have
 - (a) same atomic number
 - (b) same electronic configuration
 - (c) nearly same atomic size
 - (d) same oxidation states.

- (iii) The electronic configuration of [Lutetium] (Lu) is
- (a) $[Xe]4f^0 5d^1 6s^2$ (b) $[Xe]4f^{14} 5d^1 6s^2$ (c) $[Xe]4f^{14} 5d^3 6s^2$ (d) $[Xe]4f^{14} 5d^4 6s^2$
- (iv) Which one of the following outer orbital configurations may exhibit the largest number of oxidation states?
 - (a) $3d^54s^1$
- (c) $3d^24s^2$
- (b) $3d^54s^2$ (d) $3d^34s^2$

The correct statement(s) among the following is/are

- (i) all *d*-block elements are metals
- (ii) all *d*-block elements form coloured ions
- (iii) all d-block elements show paramagnetic behaviour.
- (a) (i) only
- (b) (i) and (ii) only
- (c) (ii) and (iii) only (d) (i), (ii) and (iii)

Read the passage given below and answer the following questions:

2. Transition elements are elements that have partially filled *d*-orbitals. The configuration of these elements corresponds to $(n-1)d^{1-10} ns^{1-2}$. It is important to note that the elements mercury, cadmium and zinc are not considered transition elements because of their electronic configurations, which corresponds to $(n-1)d^{10} ns^2$. These elements can form coloured compounds and ions due to d-d transition. These elements exhibit many oxidation states. A large variety of ligands can bind themselves to these elements, due to this, a wide variety of stable complexes formed by these ions. The boiling and melting points of these elements are high. These elements have a large ratio of charge to the radius.

In these questions (Q. No. (i)-(iv)), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- **Assertion**: Tungsten has very high melting point. **Reason**: Tungsten is a covalent compound.
- (ii) Assertion: Zn, Cd and Hg are normally not considered transition metals.

Reason: d-Orbitals in Zn, Cd and Hg elements are completely filled, hence these metals do not show the general characteristic properties of the transition elements.

- (iii) Assertion: Copper metal gets readily corroded in acidic aqueous solution such as HCl and dil. H₂SO₄. Reason: Free energy change for this process is positive.
- (iv) Assertion: Tailing of mercury occurs on passing ozone through it.

Reason: Due to oxidation of mercury.

OR

Assertion: Transition metals are poor reducing agents.

Reason: Transition metals have high enthalpies of atomisation.

Following questions (Q. No. 3-11) are multiple choice questions carrying 1 mark each:

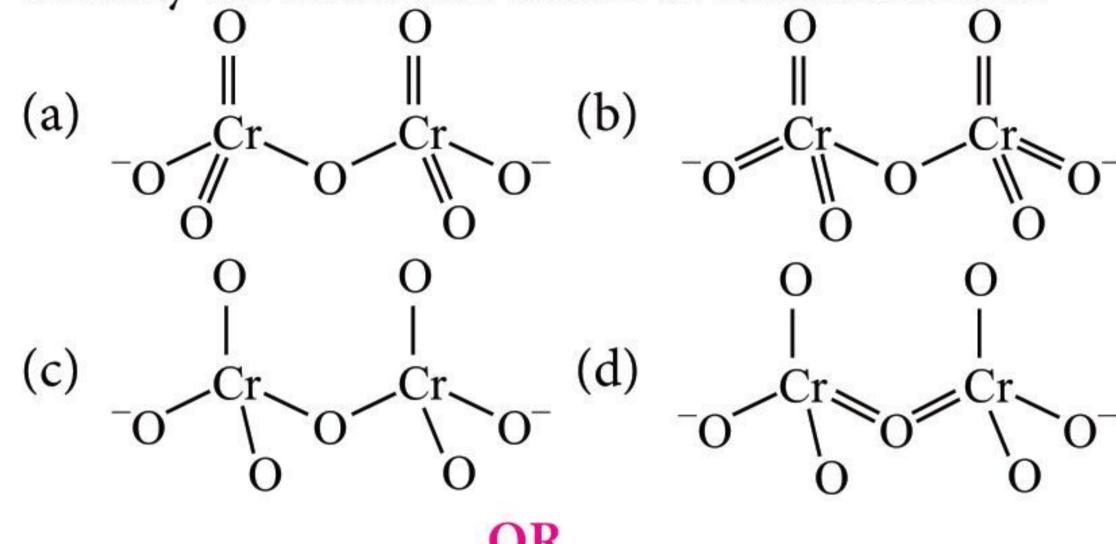
- Which of the following statements is correct?
 - (a) Titanium exhibits +6 oxidation state.
 - (b) The atomic radius of Cr is greater than that of V.
 - (c) +4 oxidation state of Sc is highly stable.
 - (d) Zinc forms colourless ion, Zn²⁺.
- Which one of the following ions have d^1 configuration?
- (a) Cr^{3+} (b) Ti^{3+} (c) Mn^{3+} (d) Fe^{3+}

The electronic configuration of Gd²⁺ is (at. no. of Gd is 64)

- (a) [Xe]4f'
- (b) [Xe] $4f^{7}5d^{1}$
- (c) [Xe] $4f^8$
- (d) [Xe] $4f^75d^16s^2$
- The colour of transition metal compounds is due to
 - (a) complete *ns*-subshell
 - (b) small size of metal ions
 - (c) incomplete (n-1)d-subshell
 - (d) absorption of light in UV region.
- A transition metal ion (M^{2+}) with atomic number 24 will have its magnetic moment
 - (a) 5.92 B.M.
- (b) 4.9 B.M.
- (c) 0 B.M.
- (d) more than 8 B.M.
- More number of oxidation state are exhibited by the actinoids than by lanthanoids. The main reason for this is
 - (a) greater metallic character of lanthanoids than that of their corresponding actinoids
 - (b) more active nature of actinoids
 - (c) more energy difference between 5f and 6d orbitals than that between 4*f* and 5*d* orbitals
 - (d) lesser energy difference between 5f and 6d orbitals than that between 4f and 5d orbitals.

In presence of acidic medium, KMnO₄ converts H_2S into

- (a) Mn only
- (b) MnS only
- (c) MnS + S
- (d) S only.
- 8. Which of the following ions does not liberate hydrogen gas on reaction with dilute acids?
 - (a) Mn^{2+}
- (b) Ti²⁺
- (c) V^{2+}
- (d) Cr^{2+}
- Identify the correct structure of dichromate ion.



The correct order of number of unpaired electrons is

- (a) $Cu^{2+} > Ni^{2+} > Cr^{3+} > Fe^{3+}$
- (b) $Ni^{2+} > Cu^{2+} > Fe^{3+} > Cr^{3+}$
- (c) $Fe^{3+} > Cr^{3+} > Ni^{2+} > Cu^{2+}$
- (d) $Cr^{3+} > Fe^{3+} > Ni^{2+} > Cu^{2+}$
- 10. Which one of the following has a magnetic moment of 1.75 B.M.?

- 11. The colour and magnetic nature of manganate ion (MnO_4^{2-}) is
 - (a) green, paramagnetic (b) purple, diamagnetic

 - (c) green, diamagnetic (d) purple, paramagnetic.

OR

Which of the following has the maximum number of unpaired *d*-electrons?

- (a) Ni^{3+}
- (b) Cu^+ (c) Zn^{2+} (d) Fe^{2+}

In the following questions (Q. No. 12-16), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- 12. Assertion: Fe^{2+} has $3d^6$ electronic configuration. **Reason**: Electrons are lost from 4s-orbital to form Fe²⁺ ion.

13. Assertion: Transition metals have high melting point.

Reason: All the transition metals have completely filled *d*-orbitals.

OR

Assertion: The correct order of oxidising power is $VO_2^+ < Cr_2O_7^{2-} < MnO_4^{-}$

Reason : The oxidation state of Mn in MnO₄ is +7.

- 14. Assertion: Mn^{2+} is more stable than Mn^{3+} . **Reason**: Mn²⁺ has half-filled configuration.
- 15. Assertion: Cu²⁺ iodide is not known. **Reason**: Cu²⁺ oxidises I⁻ to iodine.
- 16. Assertion: Members of 4d and 5d series of transition elements have nearly same atomic radii. Reason: Atomic and ionic radii for transition elements are smaller than their corresponding s-block elements.

SECTION - B

The following questions, Q. No. 17-25 are short answer type and carry 2 marks each.

- 17. Calculate the spin-only moment of Co^{2+} (Z = 27) by writing the electronic configuration of Co and Co²⁺.
- 18. What is lanthanoid contraction? What are its two consequences?

OR

- Why is europium(II) is more stable than cerium(II)?
- (b) Transition elements show high melting points. Why?
- 19. Give reasons for the following:
 - Transition metals form alloys.
 - (ii) Mn_2O_3 is basic whereas Mn_2O_7 is acidic.
- 20. (i) How is the variability in oxidation states of transition metals different from that of the *p*-block elements?
 - (ii) Out of Cu⁺ and Cu²⁺, which ion is unstable in aqueous solution and why?

Account for the following:

- (i) Transition metals show variable oxidation states.
- (ii) Zn, Cd and Hg are soft metals.
- 21. Complete the following chemical equations:
 - (i) $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow$ (ii) $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow$

OR

Assign reasons for the following:

Orange colour of Cr₂O₇²⁻ ion changes to yellow when treated with an alkali.

- (ii) Transition metals are much harder than the alkali metals.
- 22. Write the balanced chemical equations involved in the preparation of KMnO₄ from pyrolusite ore (MnO₂).
- 23. How would you account for the following:
 - (i) Actinoid contraction is greater than lanthanoid contraction?
 - (ii) Actinoids show a wide range of oxidation states then lanthanoids.
- **24.** Write the balanced ionic equations showing the oxidising action of acidified dichromate $(Cr_2O_7^{2-})$ solutions with (i) iron(II) ion and (ii) iodide ion.
- 25. With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids.

SECTION - C

- Q. No. 26-30 are short answer type II carrying 3 marks each.
- 26. Explain the following observations.
 - (i) La³⁺ and Lu³⁺ do not show any colour in solution.
 - (ii) Ce(III) is easily oxidised to Ce(IV).
 - (iii) What would happen if lanthanoid elements are treated with carbon?

OR

Explain the method of preparation of sodium dichromate from chromite ore. Give the equation representing oxidation of ferrous salts by dichromate ion.

- 27. (i) Silver atom has completely filled *d*-orbitals in its ground state, it is still considered to be a transition element. Justify the statement.
 - (ii) Why are $E_{M^{2+}/M}^{\circ}$ values of Mn and Zn more negative than expected?
 - (iii) Eu²⁺ is a strong reducing agent.
- 28. Following ions are given:

Cr²⁺, Cu²⁺, Cu⁺, Fe²⁺, Fe³⁺, Mn³⁺ Identify the ion which is

- (i) a strong reducing agent.
- (ii) unstable in aqueous solution.
- (iii) a strong oxidising agent. Give suitable reason in each.
- 29. Complete the following reactions.
 - (i) $MnO_2 + KOH + O_2 \longrightarrow$
 - (ii) $I^- + MnO_4^- + H^+ \longrightarrow$
 - (iii) $C_2O_4^{2-} + MnO_4^- + H^+ \longrightarrow$

OR

Give reasons for the following:

- (i) When SO₂ is passed through acidified K₂Cr₂O₇ solution, green Cr₂(SO₄)₃ is formed.
- (ii) $E^{\circ}_{M^{2+}/M}$ values are not regular for first row transition metals (3*d*-series).
- (iii) The enthalpies of atomization of the transition metals are high.
- 30. Assign reasons for the following:
 - (a) Actinoid contraction is greater than the lanthanoid contraction.
 - (b) The chemistry of actinoids is not as smooth as that of lanthanoids.
 - (c) Actinoids show irregularities in their electronic configurations.

SECTION - D

Q. No. 31-33 are long answer type carrying 5 marks each.

- 31. Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:
 - (i) electronic configuration
 - (ii) oxidation states
 - (iii) ionisation enthalpies and
 - (iv) atomic sizes.

OR

Assign suitable reasons for the following:

- (i) The Mn²⁺ compounds are more stable than Fe²⁺ towards oxidation to their +3 state.
- (ii) In the 3*d* series from Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomization of Zn is the lowest.
- 32. How do the oxides of transition elements in lower oxidation states differ from those in higher oxidation states and why?

OR

Describe the preparation of potassium dichromate from chromite ore. What is the effect of change of pH on dichromate ion?

- 33. How would you account for the following:
 - (i) Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.
 - (ii) There is a gradual decrease in the size of atoms with increasing atomic number in the series of lanthanoids.

The elements of 3*d* transition series are given as : Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn Answer the following :

- (i) Which element has highest melting point?
- (ii) Which elements have less negative E° value than that of Cr?
- (iii) Which element is not considered as transition element?
- (iv) Which element shows maximum oxidation state of +6?
- (v) Which element is a strong reducing agent in +2 oxidation state?

SOLUTIONS

1. (i)(b)

(ii) (c): Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals.

(iii)(b)

(iv) (b): Greater the number of valence electrons, more will be the number of oxidation states exhibited by the element.

OR

- (a): All the d-block elements are metals, they exhibit most properties of metals like lustre, malleability, ductility, high density, high melting and boiling point, hardness, conduction of heat and electricity, etc. When an electron from a lower energy d-orbital is exited to a higher energy d-orbital, the energy of excitation corresponds to frequency of light absorbed. Due to the presence of unpaired electrons, they show paramagnetic behaviour.
- 2. (i)(c): Tungsten is a transition element and is very hard due to strong metallic bonding.

(ii) (a)

- (iii)(d): Non-oxidising acids (HCl and dil. H_2SO_4) do not have any effect on copper. However they dissolve the metal in presence of air. As it is a non-spontaneous process so, ΔG cannot be –ve.
- (iv) (a): When mercury is exposed to ozone it gets superficially oxidised and loses its meniscus and sticks to the glass.

OR

(b)

3. (d): Zinc forms colourless ions because it does not have unpaired d-electrons in its orbitals.

4. **(b)**:
$$Cr^{3+}(d^3) - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$$

 $Ti^{3+}(d^1) - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

$$\operatorname{Mn}^{3+}(d^4) - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$$

 $\operatorname{Fe}^{3+}(d^5) - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

(d).: Acidified KMnO₄ oxidises H₂S to S only. $2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$

OR

- 8. (a): The third ionisation energy of Mn is too high due to stable half filled 3d-orbital. Hence, it cannot further get oxidised to liberate hydrogen.
- 9. (a)

OR

- (c): $Fe^{3+} 3d^5$ No. of unpaired electrons = 5 $Cr^{3+} - 3d^3$ No. of unpaired electrons = 3 $Ni^{2+} - 3d^8$ No. of unpaired electrons = 2 $Cu^{2+} - 3d^9$ No. of unpaired electrons = 1
- 10. (a): Magnetic moment $(\mu) = \sqrt{n(n+2)}$ B.M. where n = number of unpaired electrons.

Ions	No. of unpaired electrons	Magnetic moment (B.M.)	
$Ti^{3+}: 3d^1 4s^0$	1	1.73	
$V^{3+}: 3d^2 4s^0$	2	2.83	
$Cr^{3+}: 3d^3 4s^0$	3	3.87	
$Fe^{3+}: 3d^5 4s^0$	5	5.92	

11. (a): Manganate ion, MnO_4^{2-} is green in colour and is paramagnetic in nature.

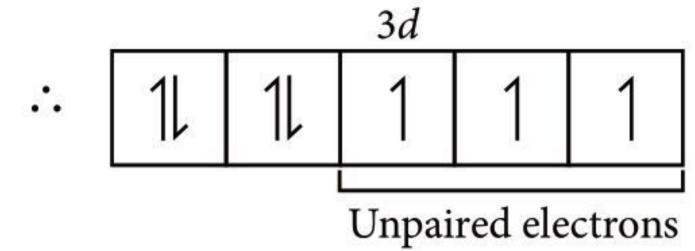
OR

(d)

OR

- (b) : The oxidation states of the given compounds are $VO_2^+: x + 2(-2) = +1 \Rightarrow x = +5$ $Cr_2O_7^{2-}: 2x + 7(-2) = -2 \Rightarrow 2x = +12 \Rightarrow x = +6$ $MnO_4^-: x + 4(-2) = -1 \Rightarrow x = -1 + 8 = +7$ The correct order of oxidising power is $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$ due to the increasing stability of the lower species to which they are reduced.
- 14. (a): A half-filled or fully-filled configuration is more stable than an incompletely filled configuration.
- 15. (a)
- 16. (b): It is due to lanthanide contraction.
- 17. (b): $Co = [Ar]3d^74s^2$

$$Co^{2+} = [Ar]3d^7$$



i.e., there are three unpaired electrons (n = 3). Hence, $\mu = \sqrt{n(n+2)}$ B. M. $= \sqrt{3(3+2)} = 3.87$ B.M.

18. Lanthanoid contraction: The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by 4*f*-electrons.

Consequences of lanthanoid contraction:

- (i) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.
- (ii) Atomic and ionic sizes of 4d transition series elements and 5*d* series elements are similar. *e.g.*, atomic radius of zirconium(Zr) is same as that of hafnium (Hf)

- (a) Europium(II) has electronic configuration [Xe]4f'5d' while cerium(II) has electronic configuration [Xe] $4f^2$. In Eu²⁺, 4f- subshell is half-filled and 5*d*-subshell is empty. Since half-filled and completely filled electronic configurations are more stable, Eu²⁺ ion is more stable than Ce²⁺.
- (b) The high melting points of transition metals are attributed to the involvement of greater number of electrons from (n - 1) d orbitals in addition to ns electrons in the interatomic metallic bonding.
- 19. (i) Transition metals form alloys because they have similar atomic radii.
- (ii) Basic nature of oxides decreases and acidic nature increases with increase in oxidation state of the metal. Oxidation state of Mn in Mn_2O_3 is +3 while in Mn_2O_7 is +7.
- 20. (i) Variable oxidation states of transition metals arise due to incomplete filling of *d*-orbitals and it differs from each other by unity e.g., $V^{(V)}$, $V^{(IV)}$, $V^{(III)}$, $V^{(III)}$. In p-block elements oxidation states differ generally by a unit of two. e.g., Sn(II), Sn(IV), PCl₃, PCl₅, etc.
- (ii) In aqueous solutions, Cu⁺ undergoes disproportionation to form a more stable Cu²⁺ ion.

$$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$$

Cu²⁺ in aqueous solutions is more stable than Cu⁺ ion because hydration enthalpy of Cu²⁺ is higher than that of Cu⁺. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu²⁺ ions.

OR

(i) Transition elements can use their (n-1)d orbital electrons for bond formation therefore, they show variable oxidation states.

For example, Sc has $ns^2(n-1)d^1$ electronic configuration. If it utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state becomes +3.

- (ii) In Zn, Cd and Hg, all the electrons in d-subshell are paired. Hence, the metallic bonds are weak. That is why they are soft metals with low melting and boiling points.
- 21. (i) $8\text{MnO}_4^- + \text{H}_2\text{O} + 3\text{S}_2\text{O}_3^{2-} \rightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-}$ $+2OH^{-}$
- (ii) $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
- (i) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when an alkali such as NaOH is added because on addition of an alkali, the concentration of H⁺ ions decreases and hence, the reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions.

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

orange yellow

- (ii) Transition metals have more number of unpaired electrons in their valence shells. As a result, they are able to form strong metallic bonds which results in extreme hardness as compared to alkali metals.
- 22. Preparation of potassium permanganate: Potassium permanganate is prepared by the fusion of MnO₂ (pyrolusite) with potassium hydroxide and an oxidising agent like KNO₃ to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

 $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

- 23. (i) The actinoid contraction is more than lanthanoid contraction because 5f-electrons are more poorly shielded than 4*f*-electrons.
- (ii) Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f* and 6*d* orbitals in actinoids than the energy difference between 4f and 5d orbitals in case of lanthanoids.

24.
$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

 $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

25. Structure: All the lanthanoids are silvery white soft metals. Hardness of Lanthanoids increases with increasing atomic number. The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is due to irregularities in metallic radii which are greater than that of lanthanoids. Chemical reactivity: Earlier members of lanthanoid series are quite reactive similar to calcium but with increasing atomic number they behave more like aluminium.

The actinoids are highly reactive in finely divided state.

- 26. (i) Because La³⁺ and Lu³⁺ do not contain any unpaired electrons.
- (ii) Ce^{3+} ions with the configuration $4f^15d^06s^0$ can easily lose electron to aquire the configuration $4f^0$ $5d^06s^0$ and form Ce^{4+} .
- (iii) Lanthanoid elements are heated with carbon to make carbides

$$Ln + C \xrightarrow{\Delta} LnC_2$$
OR

Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore (FeCr₂O₄) with sodium or potassium carbonate in free excess of air as follows:-

$$4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$$

The yellow solution of sodium chromate is acidified with sulphuric acid to give a orange solution of sodium dichromate Na₂Cr₂O₇ which is crystallised.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Sodium
chromate Sodium
dichromate

The solution of sodium dichromate is treated with potassium chloride to obtain potassium dichromate.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Potassium
dichromate

$$Cr_2O_{7(aq)}^{2-} + 14H_{(aq)}^+ + 6Fe_{(aq)}^{2+} \rightarrow 2Cr_{(aq)}^{3+} + 6Fe_{(aq)}^{3+} + 7H_2O_{(l)}$$

- 27. (i) Silver atom has outer electronic configuration $4d^{10}5s^1$ in its ground state, but silver in +2 oxidation state has electronic configuration $4d^9$. So in +2 oxidation state, silver has incomplete d-orbital. Hence, silver is considered as a transition element.
- (ii) Mn^{2+} ion has stable half-filled (3 d^5) electronic configuration whereas Zn^{2+} has completely filled d^{10} configuration. Hence, $E_{\text{Mn}^{2+}/\text{Mn}}^{\circ}$ and $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$ are more negative than expected.
- (iii) Eu²⁺ has a strong tendency to loose electrons to attain the more stable +3 oxidation state of lanthanoids hence, it is a strong reducing agent.
- 28. (i) Cr²⁺ is a strong reducing agent since its configuration is converted to d^3 from d^4 . d^3 has half filled t_{2g} configuration with higher stability.
- (ii) Cu⁺ is unstable in aqueous solution.

In aqueous solutions, Cu⁺ undergoes disproportionation to form a more stable Cu²⁺ ion.

$$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$$

(iii) Mn³⁺ is a strong oxidising agent because electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, i.e., 3rd electron cannot be lost easily.

29. (i)
$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

(ii)
$$10I^{-} + 2MnO_{4}^{-} + 16H^{+} \longrightarrow 2Mn^{2+} + 8H_{2}O + 5I_{2}$$

(iii)
$$5C_2O_4^{2-} + 2MnO_4^{-} + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

(i) (d):
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

- (ii) The $E_{M^{2+}/M}$ values are not regular which can be explained from the irregular variation of ionisation enthalpes i.e., $IE_1 + IE_2$ and also the sublimation enthalpies which are relatively much less for manganese and vanadium.
- (iii) As transition metals have a large number of unpaired electrons in the *d*-orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.
- 30. (a) The actinoid contraction is more than lanthanoid contraction because 5*f*-electrons are more poorly shielded than 4*f*-electrons.
- (b) The chemistry of actinoids is not as smooth as lanthanoid because they show greater number of oxidation states due to comparable energies of 5f, 6d and 7s orbitals.
- (c) The irregularities in the electronic configurations of actinoids are due to extra stabilities of the f^0 , f^7 and f^{14} orbitals.
- Electronic configuration : Electronic configuration of group 3 elements (Sc, Y, La) is [Noble gas] $(n-1)d^{1} ns^{2}$.

Elements of group 6 (Cr, Mo and W) show exception in electronic configuration. For Cr and Mo [Noble gas]

 $(n-1)d^5 ns^1$ and for W it is [Noble gas] $4f^{14} 5d^4 6s^2$.

Group 11 elements (Cu, Ag and Au) also show exceptional electronic configuration:

$$Cu = [Ar] 3d^{10} 4s^1, Ag = [Kr] 4d^{10} 5s^1,$$

$$Au = [Xe]4f^{14} 5d^{10} 6s^1.$$

Group - 10 (Ni, Pd and Pt) also show anomalous electronic configuration:

Ni - [Ar]
$$3d^8 4s^2$$
 Pd - [Kr] $4d^{10} 5s^0$

Pt - [Xe]
$$4f^{14} 5d^9 6s^1$$

(ii) Oxidation states: Elements within the same group show similar oxidation states. Highest number of oxidation states are shown by the elements lying in the middle of the transition series. Minimum oxidation states are shown by the elements lying near to left and far right side of the series. Stability of higher oxidation states increases from first to third series.

- (iii) Ionisation enthalpies : Ionisation enthalpies generally decrease down a group. This trend is followed from 3d to 4d-elements but the ionisation enthalpies either remain same or increase in going from 4d to 5d-series with in the same group. This reverse trend is due to the poor shielding of the nuclear charge by the inner 4f-electrons. This increases the Z_{eff} and in turn increases the ionisation enthalpy.
- (iv) Atomic size: Due to poor shielding of nuclear charge by 4f-electrons, increase in Z_{eff} decreases the size. So, the atomic size increase from 3*d* to 4*d* but decrease or remain almost the same from 4d to 5d.

- (i) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, i.e., 3rd electron cannot be lost easily. In case of Fe^{2+} , electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.
- (ii) Zinc (Z = 30) has completely filled d-orbital ($3d^{10}$), so *d*-orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.
- 32. In the lower oxidation state, the transition metal oxides are basic and they are acidic if the metal is in higher oxidation state. The oxides are amphoteric when the metal is in intermediate oxidation state. For example,

In case of lower oxide of a transition metal, the metal atom has a low oxidation state. This means some of the valence electrons of the metal atom are not involved in bonding, hence, these can be used for donation. Thus, these are act as bases.

OR

$$4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 8\text{Na}_2\text{CrO}_4 + \\ 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$$

$$2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \longrightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$$

$$\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \longrightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$$

Potassium dichromate is converted to chromate if pH is increased.

$$\operatorname{Cr}_2\operatorname{O}_7^{2-} \xrightarrow{\operatorname{OH}^-} \operatorname{Cr}\operatorname{O}_4^{2-}$$

33. (i) Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states

in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty $(4f^0)$, half-filled $(4f^7)$ and fully filled $(4f^{14})$ sub shell.

e.g.,
$$Ce^{4+}:4f^{0}$$
, $Eu^{2+}:4f^{7}$
 $Tb^{4+}:4f^{7}$, $Yb^{2+}:4f^{14}$

(ii) As the atomic number increases, each succeeding element contains one more electron in the 4f orbital and one extra proton in the nucleus. The 4f electrons are rather ineffective in screening the outer electrons from the nucleus. As a result, there is gradual increase in the nuclear attraction for the outer electrons. Consequently, the atomic size gradually decreases. This is called lanthanoid contraction.

- (i) Cr has highest melting point.
- (ii) The E° values of Ti, V and Mn are less negative than *E*° value of Cr.
- (iii) Zn metal is not considered as transition element because it has fully-filled *d*-orbital.
- (iv) Cr shows maximum oxidation state of +6 in its compounds.
- (v) Cr is strong reducing agent in +2 oxidation state.



Computational study says polonium can form hydrogen bonds!

ydrogen bonds are non-covalent interactions that are prevalent in biomolecular chemistry and understanding them can help to explain the complex biological processes and systems. Conventionally, hydrogen bonding is thought to be caused by a difference in electronegativities between the interacting atoms. Indian scientists uncovered that the strength of $X-H\cdots S/Se$ hydrogen bonds was down to polarizability and dispersion. Using Density Functional Theory (DFT), they have shown how $X-H\cdots$ Po hydrogen bonds can form, using Me₂Po as the hydrogen bond donor. Strength-wise, the X-H···Po hydrogen bond is comparable to conventional hydrogen bonds (10–30 kJ mol⁻¹). They also performed two component relativistic, DFT calculations and discovered that, unlike other chalcogen complexes, the relativistic effect influences hydrogen bonding in polonium complexes.

MONTHLY TEST

his specially designed column enables students to self analyse their extent of understanding the specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Aldehydes, Ketones and Carboxylic Acids | Amines Time Taken: 60 Min. **Total Marks: 120**

NEET

Only One Option Correct Type

- 1. Calcium acetate when dry distilled gives
 - (a) formaldehyde (b) acetaldehyde
 - (c) acetone
- (d) acetic anhydride.
- 2. Which of the following carboxylic acids undergoes decarboxylation easily?
 - (a) $C_6H_5 CO CH_2 COOH$
 - (b) $C_6H_5 CO COOH$
 - (c) C_6H_5 —CH—COOHOH
 - (d) C_6H_5 —CH—COOH NH_2
- Which of the following amines gives carbylamine reaction?
 - (a) $C_2H_5NH_2$
- (b) $(C_2H_5)_2NH$
- (c) $(C_2H_5)_3N$
- (d) $CH_3NHC_2H_5$
- In nucleophilic addition reactions the reactivity of carbonyl compounds follows order
 - (a) $H_2C = O > R_2C = O > Ar_2C = O > RCHO$

> ArCHO

(b) $H_2C = O > RCHO > ArCHO > R_2CO$

> Ar₂C = O

(c) $Ar_2C = O > R_2C = O > ArCHO > RCHO$

 $> H_2C = O$

(d) ArCHO > Ar₂C = O > RCHO > R_2 C = O

 $> H_2C = O$

- Diethylamine reacts with nitrous acid to give
 - (a) $(C_2H_5)_2NH^+NO_2^-$ (b) $(C_2H_5)_2NNO_2^-$
 - (c) C_2H_5OH
- (d) N₂ and alcohol

- A compound which gives a yellow solid on adding to an alcoholic solution of 2,4-dinitrophenylhydrazine but does not reduce Fehling's solution and ammoniacal silver nitrate solution, is
 - (a) CH₃CH(OH)CH₃ (b) CH₃COCH₃

 - (c) CH₃CHO (d) CH₃COOH
- 7. Propan-2-ol on treatment with copper at 300°C forms
 - (a) acetone
- (b) acetaldehyde
- (c) ethane
- (d) both (a) and (b).
- The compound $C_5H_{13}N$ is optically active and reacts with HONO to give $C_5H_{11}OH$. The compound is
 - (a) N-methylbutanamine

 - (b) 2-aminopentane (c) 1-aminopentane
 - (d) N, N-dimethylpropanamine.
- Chloropicrin is obtained by the reaction of
 - (a) steam on carbon tetrachloride
 - (b) nitric acid on chlorobenzene
 - chlorine on picric acid
 - (d) nitric acid on chloroform.
- 10. The IUPAC name of the compound

- (a) 2-(carboxymethyl)pentane-1,5-dioic acid
- (b) 3-carboxyhexane-1,6-dioic acid
- (c) butane-1,2,4-tricarboxylic acid
- (d) 4-carboxyhexane-1,6-dioic acid.
- 11. The reagents needed for the following conversion is

- (a) KOH, Br₂; LiAlH₄
- (b) KOH, Br₂; CH₃COCl
- (c) HONO, Cu₂Cl₂, (CH₃CO)₂O
- (d) KOH, Br₂; Ni, H₂, CH₃COCl
- 12. Which reaction is suitable for preparing α -chloroacetic acid?
 - (a) Hell-Volhard-Zelinsky reaction
 - (b) Stephen's reaction
 - (c) Perkin's reaction
 - (d) None of these

Assertion & Reason Type

Directions: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- **13. Assertion**: Alkyl cyanides and alkyl isocyanides have much higher boiling points than corresponding alkyl halides.

Reason: Cyanides and isocyanides are much more polar than alkyl halides.

14. Assertion : Cross Cannizzaro's reaction between methanal and benzaldehyde gives benzyl alcohol and formate ion.

Reason: Benzaldehyde does not contain α-hydrogen atom.

15. Assertion : *R*CHO, *R*COCH₃ and cyclic ketones react with sodium bisulphite.

Reason: Crystalline solid derivatives are formed when aldehydes or ketones are shaken with saturated aqueous solution of sodium bisulphite.

JEE MAIN / JEE ADVANCED

Only One Option Correct Type

16. End product of the following sequence of reaction is

$$CH_3 \xrightarrow{(i) I_2 + NaOH, \Delta}$$

$$CH_3 \xrightarrow{(ii) H^+, \Delta}$$

COOH

(a) Yellow precipitate of CHI₃,

(d) Yellow precipitate of CHI₃, COOH

17. The major product of the following reaction is

$$\begin{array}{c} & (i) \text{ KOH, H}_2\text{O} \\ \hline & (ii) \text{ H}^+, \text{ Heat} \\ \end{array}$$

$$\begin{array}{c} \text{CH}_3 \\ \text{(a)} \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{(b)} \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{O} \end{array}$$

$$\text{(c)} \qquad \begin{array}{c} \text{CH}_3 \\ \text{(d)} \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array}$$

18. What is the product obtained in the following reaction?

$$(a) \bigcirc NO_{2} \xrightarrow{NH_{4}Cl}$$

$$(a) \bigcirc NO_{2} \xrightarrow{NH_{4}Cl}$$

$$(b) \bigcirc NO_{2} \xrightarrow{NH_{4}Cl}$$

$$(c) \bigcirc NO_{2} \xrightarrow{NH_{4}Cl}$$

$$(d) \bigcirc NH_{2}$$

19. In the following reaction sequence, the compound *J* is an intermediate.

$$I \xrightarrow{\text{(CH}_3\text{CO)}_2\text{O}} J \xrightarrow{\text{(i) H}_2, \text{Pd/C}} K$$

$$\xrightarrow{\text{(ii) SOCl}_2} K$$

$$\text{(iii) anhyd.AlCl}_3$$

J (C₉H₈O₂) gives effervescence on treatment with NaHCO₃ and a positive Baeyer's test.

The compound I is

More than One Option Correct Type

- 20. A positive carbylamine test is given by
 - (a) *N*, *N*-dimethyl aniline
 - (b) 2, 4-dimethyl aniline
 - (c) *N*-methyl-*o*-methyl aniline
 - (d) *p*-methyl benzylamine.
- 21. Which of the following reactions will form ethyl ethanoate?
 - (a) $CH_3COCl + C_2H_5OH \longrightarrow$

 - (b) $C_6H_5COCl + C_2H_5OH \xrightarrow{Al(OC_2H_5)_3}$ (c) $CH_3CHO + CH_3CHO \xrightarrow{Al(OC_2H_5)_3}$
 - (d) $(CH_3CO)_2O + C_2H_5OH \longrightarrow$
- 22. $2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+[BH_4]^-$ The amine(s) X is/are
 - (a) NH_3
- (b) CH_3NH_2
- (c) $(CH_3)_2NH$
- (d) $(CH_3)_3N$

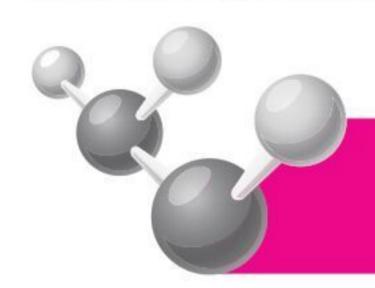
- 23. Which of the following statements about benzaldehyde is/are correct?
 - (a) Reduces Tollen's reagent
 - (b) Undergoes Aldol condensation
 - (c) Undergoes Cannizzaro's reaction
 - (d) Does not form addition compound with sodium hydrogen sulphide

Integer / Numerical Value Type

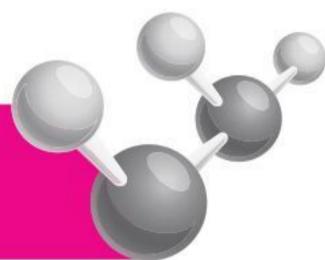
24. Complete the following reaction sequence and find the number of benzene rings in compound (D).

COOH
$$\xrightarrow{\text{PCl}_5} A \xrightarrow{\text{O}, \text{AlCl}_3} B \xrightarrow{\text{MgBr}} D$$

$$\xrightarrow{\text{C}_2\text{H}_5\text{OH, H}^+} C$$



3 Amazing Facts You Must Know



1. Why Do Fresh Eggs Sink, and Rotten Eggs Float?

A classical trick to know whether we can still eat an egg (if they are fresh enough) is putting them in a bowl of water. If the egg sinks, it means that it is still denser than water, which is the natural state if they are fresh. As decomposition takes place, solid and liquid matter is transformed into gas. Gaseous pressure builds up, and since the egg shell is porous, this gas starts escaping. This loss of mass, eventually leads to the density of the egg becoming lower than that of water. This makes the egg float on water.



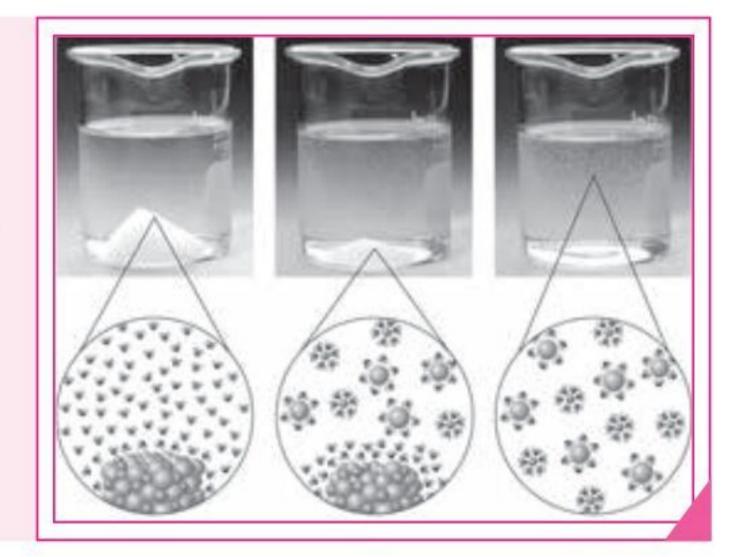
2. Do Frogs Need to Drink?

Frogs do not need to drink using their mouths. They absorb water through their skin. They have a skinarea called "drinking patch", on their bellies, which they use to get all the water they need.



3. What Happens to the Volume of Water when You Add Table Salt to It?

Volumes are not always additive. When you add table salt, or NaCl to water, you are increasing the density of water. This happens due to positive interactions between water molecules and Na⁺ and Cl⁻ ions. Since the resulting mixture is denser, the total volume will decrease and become lower than the actual sum of volume of water and volume of the added salt.



25. The number of products in the given reaction will be deuterated is _____.

$$D$$

$$|$$

$$2H-C=O+OH^{-}\longrightarrow$$

26. The minimum number of nitrogen atoms that must be present in the compound whose one molecule contains 7 carbon atoms, 1 chlorine atom and 7 hydrogen atoms is _____.

Comprehension Type

Nitrogen atom of amines has a lone pair of electrons, thus, amines behave as Lewis bases. Amines have a tendency to accept proton from acids. Basic strength of different amines is compared on the basis of their K_h values (basicity constant) or pK_h

$$K_b = \frac{[R \mathring{N} H_3][OH^-]}{[RNH_2]}$$

$$pK_b = -\log K_b = \log \frac{1}{K_b}$$

Smaller the value of pK_b , or greater the value of K_b , stronger is the base.

- 27. The order of basic strength among the following amines in benzene solution is
 - (a) $CH_3NH_2 > (CH_3)_3N > (CH_3)_2NH$
 - (b) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
 - (c) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
 - (d) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$
- 28. Which of the following is least basic?

(a)
$$O_2N - \bigcirc \longrightarrow NH_2$$

(b) $CH_3O - \bigcirc \bigcirc \longrightarrow NH_2$

(c)
$$H_5C_6$$
 \longrightarrow NH_2

(d)
$$EtO_2C - \left(\bigcirc \right) - NH_2$$

Matrix Match Type

29. Match the column I with column II and select the correct option.

	Column I		Column II
(A)	C ₆ H ₅ CHO	(p)	Aldol condensation
(B)	O CH ₃ CCH ₃	(q)	Reformatsky reaction
(C)	O C—OEt/OEt	(r)	Perkin's reaction
(D)	BrCH ₂ COOC ₂ H ₅ + Zn	(s)	Claisen condensation

- (a) A (p), B (q), C (s), D (r)
- (b) A (r), B (s), C (q), D (p)
- (c) A (r), B (p), C (s), D (q)
- (d) A (s), B (p), C (r), D (q)
- 30. Match the column I with column II and select the correct option.

	Column I	9	Column II
	(Amines)		(Characteristics)
(A)	CH ₃ CH ₂ CH ₂ NH ₂	(p)	Treatment of
			NaNO ₂ , HCl gives
			N-nitroso compound
(B)	CH ₃ CH ₂ NHCH ₃	(q)	Treatment of
			NaNO ₂ , HCl gives
			diazonium chloride
(C)	CH_3 — N — CH_3	(r)	Treatment of CH ₃ I
	CH		(excess) followed by
	CH_3		AgOH; heat gives
			out alkene
(D)	<u>/</u>	(s)	Treatment of HCl
Accepted Village	NH_2	500 VID	followed by heating
			gives dealkylation

- (a) A (q), B (p, s), C (p, q, r), D (s)
- (b) A (p, s), B (q, r), C (q, r), D (r)
- (c) A (p), B (q, r, s), C (q), D (q)
- (d) A (r, s), B (p, r, s), C (s), D (q)

⋄ ⋄

.....

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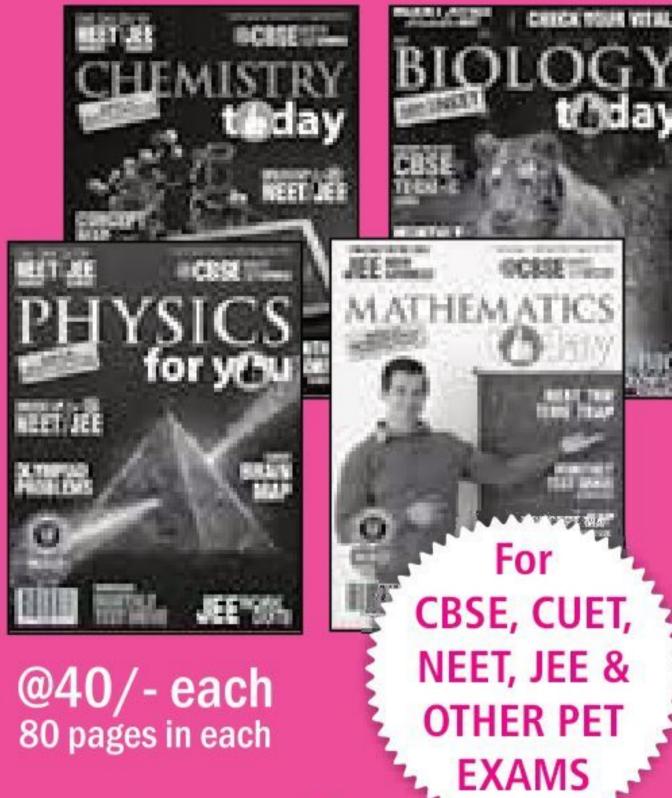
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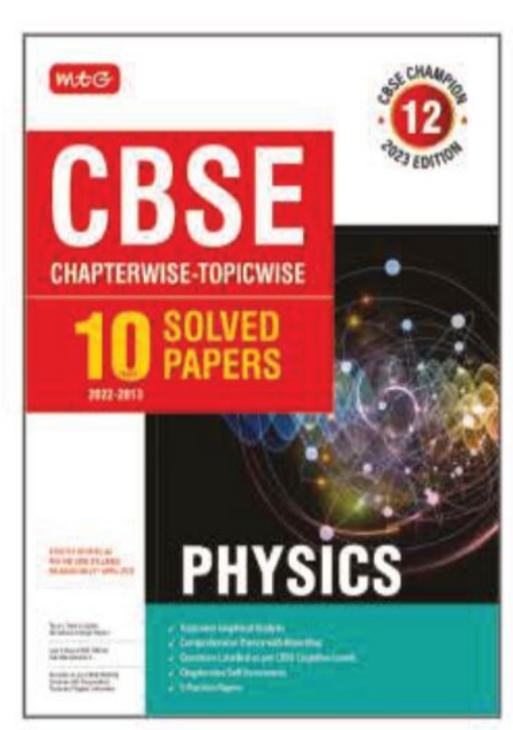
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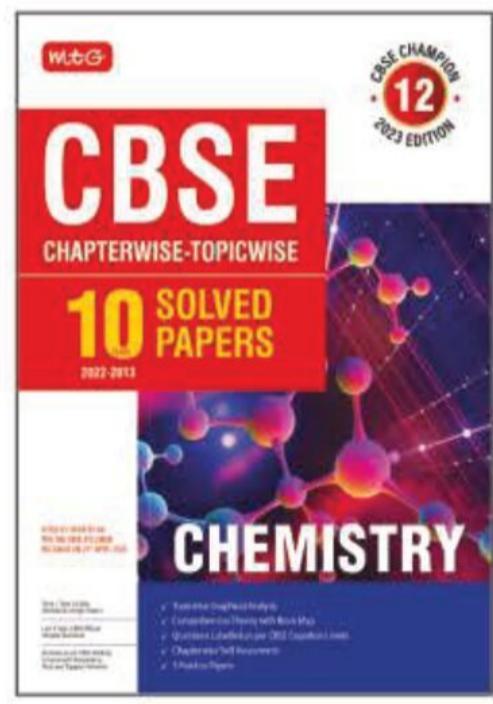


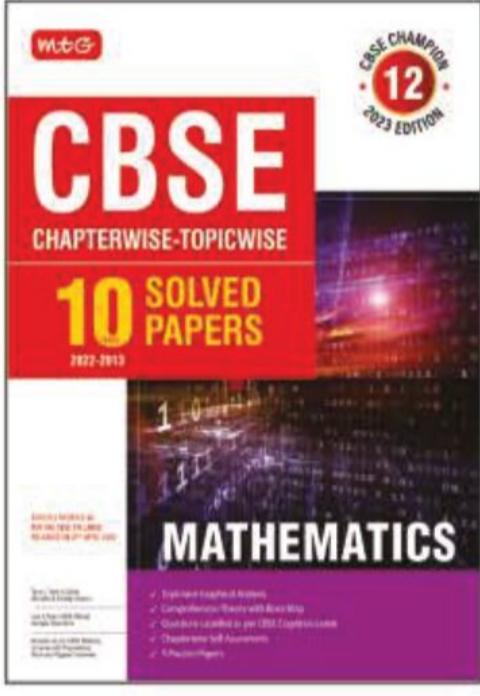
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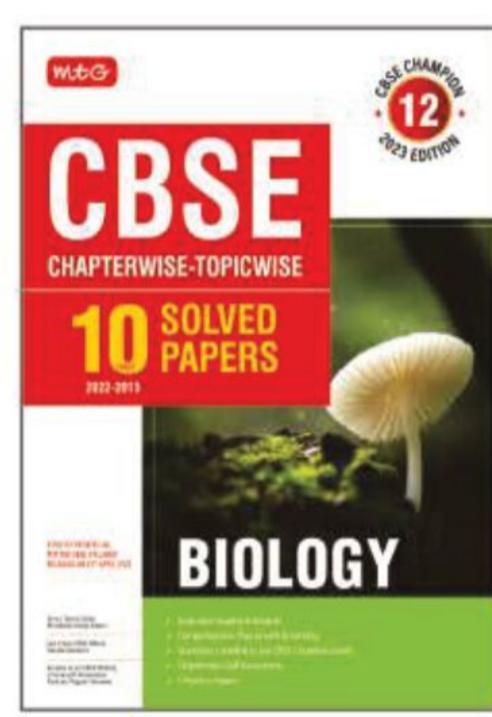


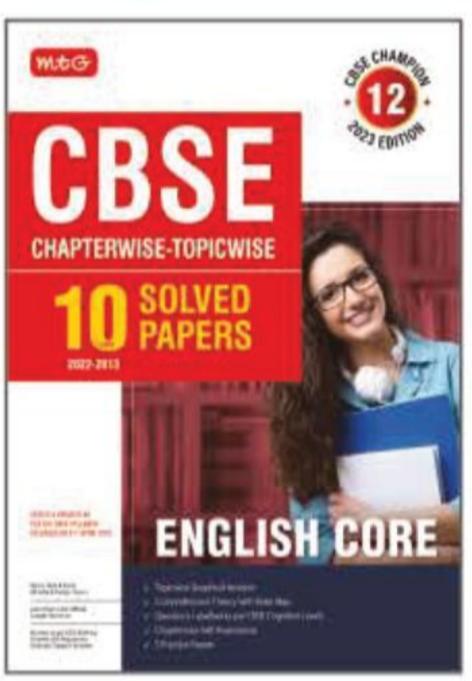
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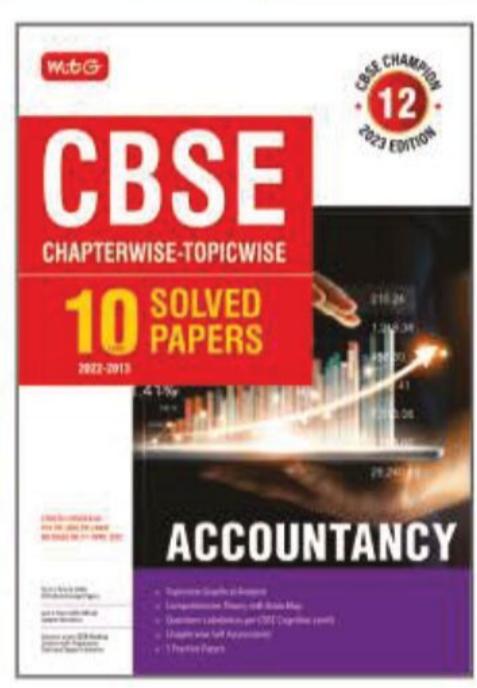


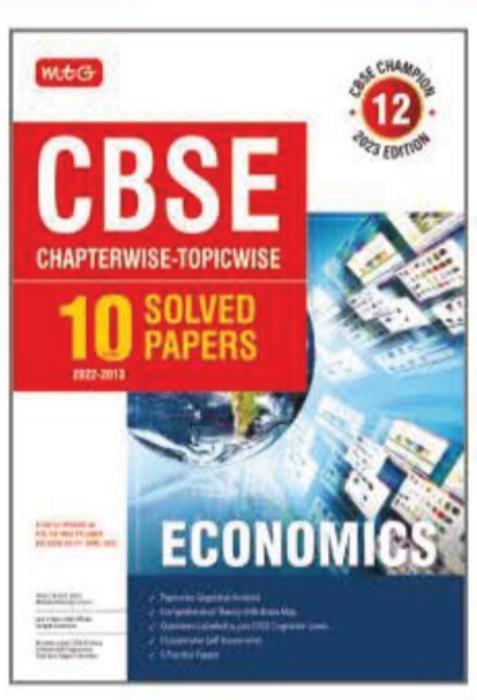


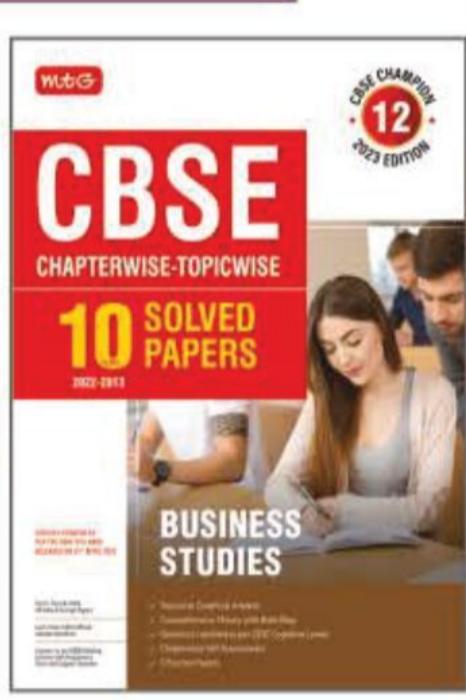


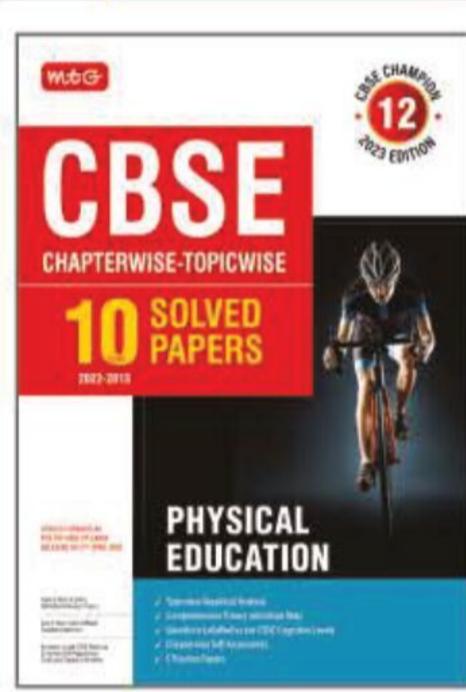


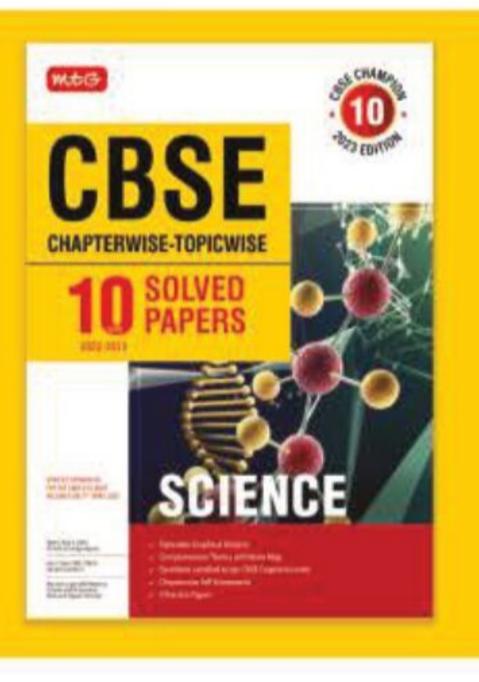


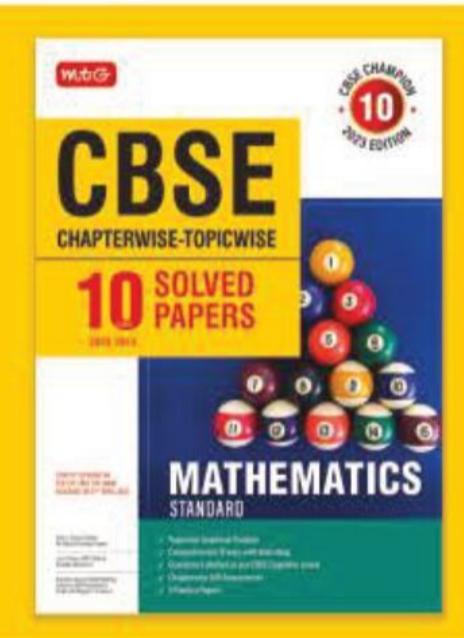


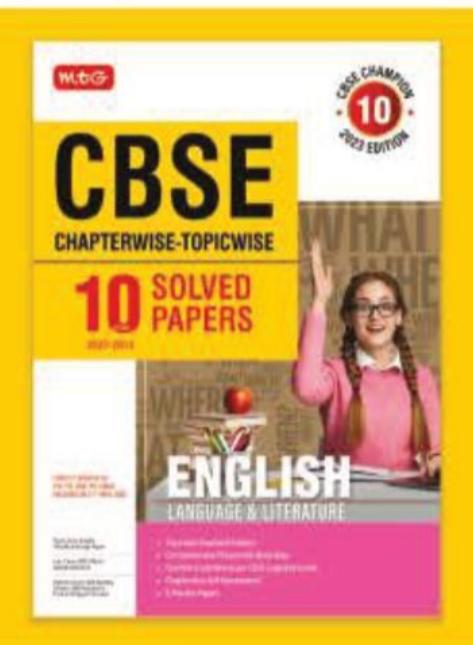


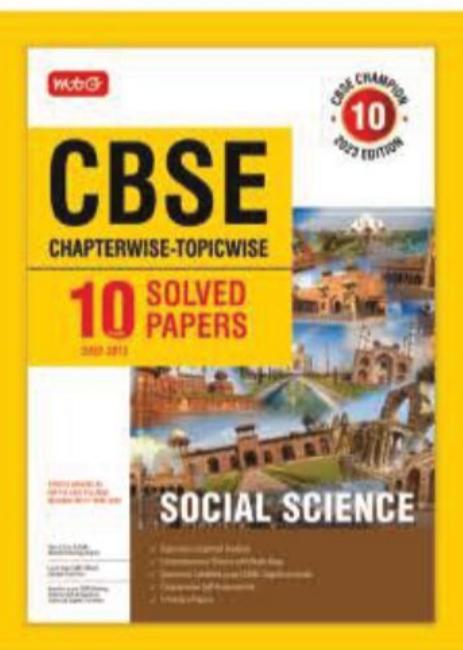


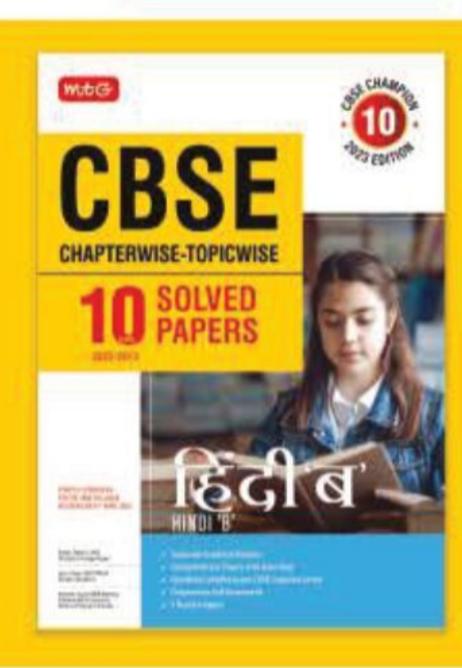












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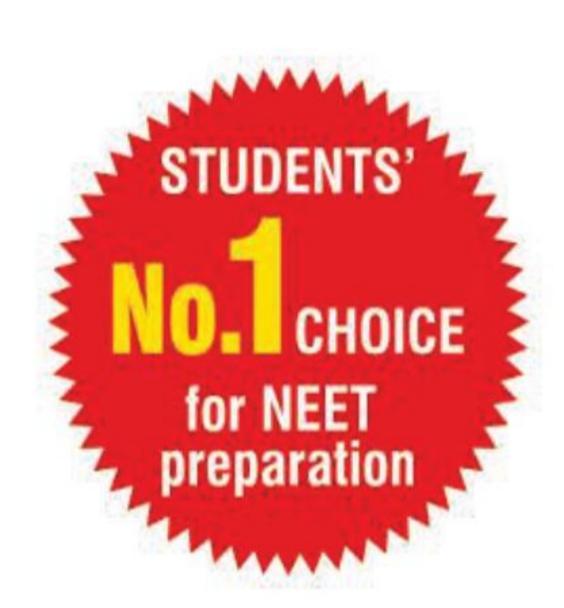
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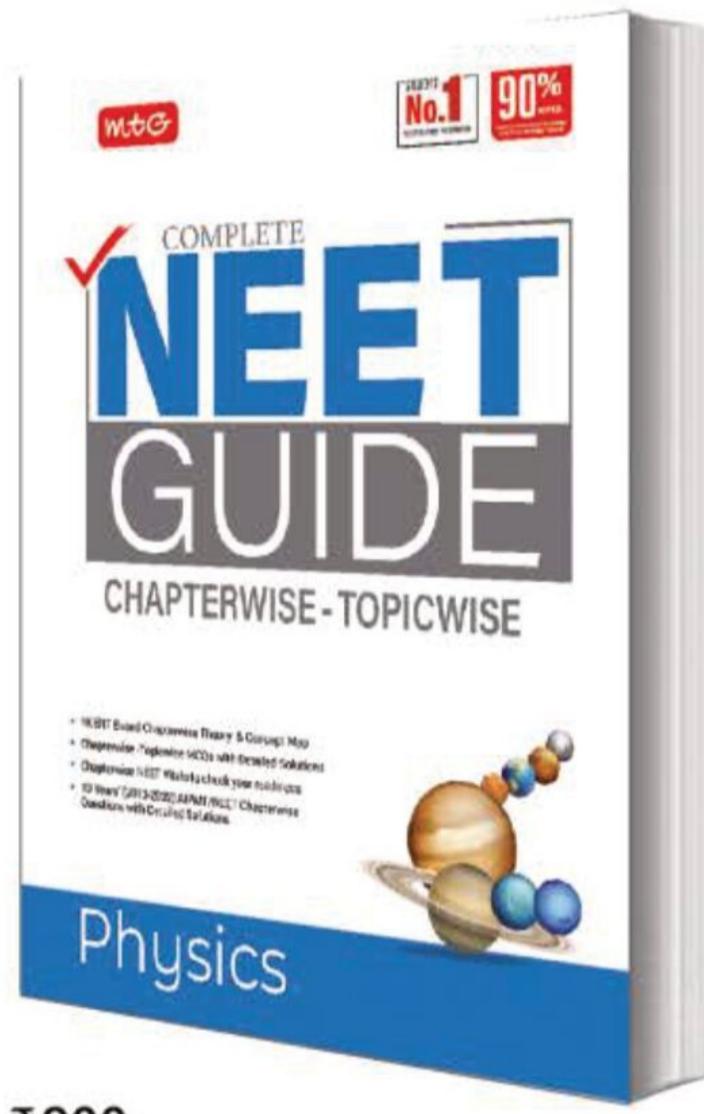
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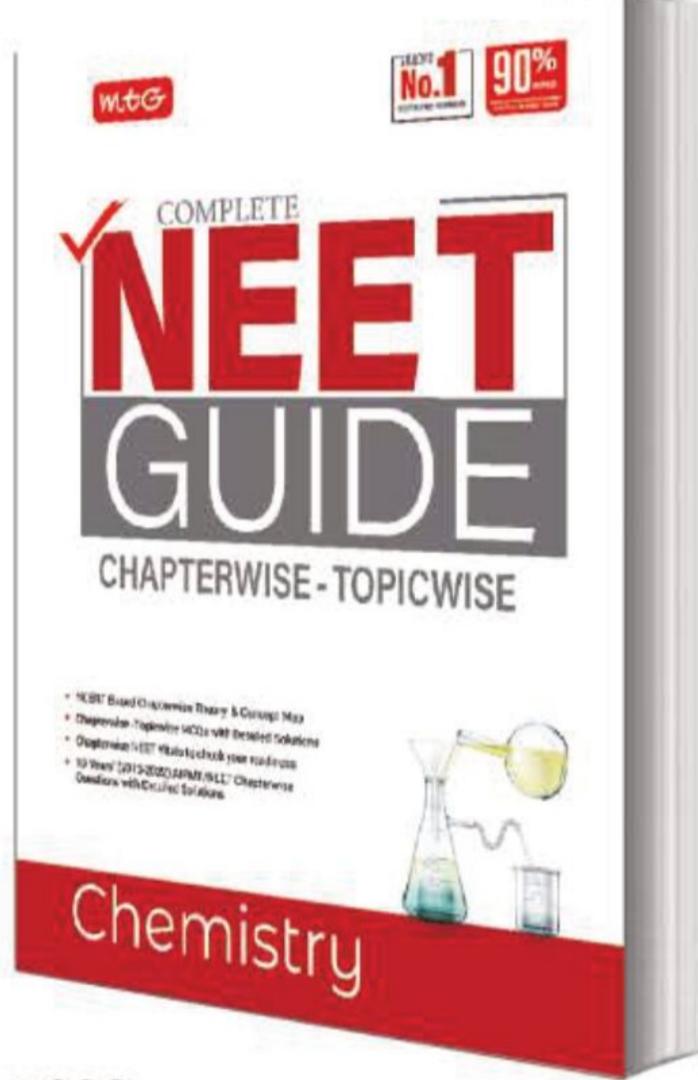


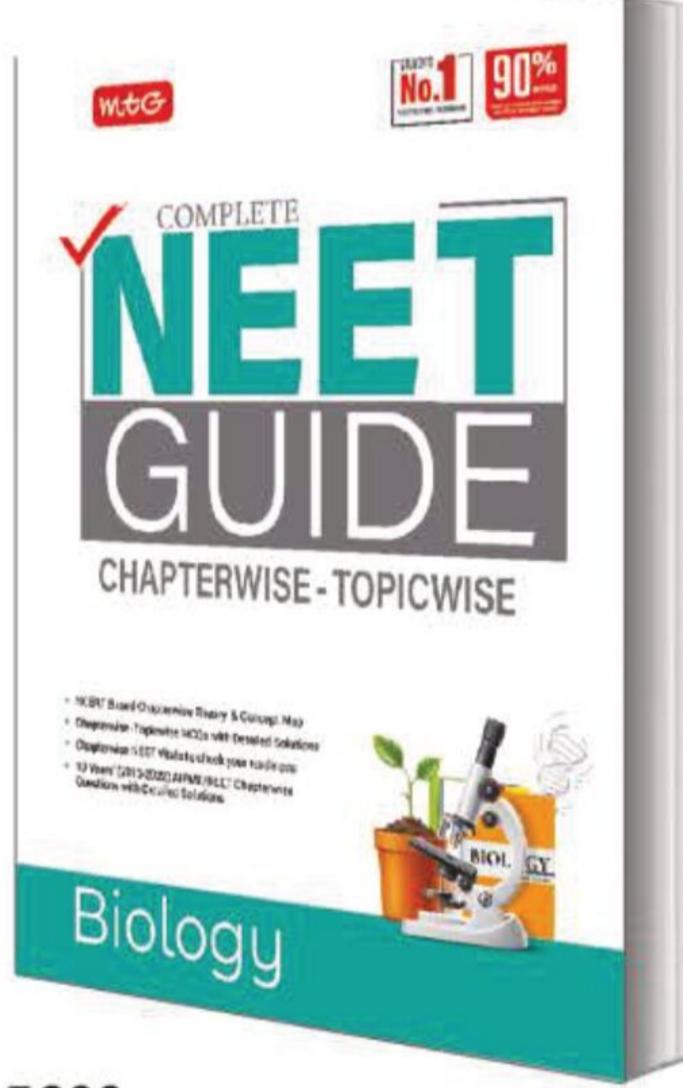
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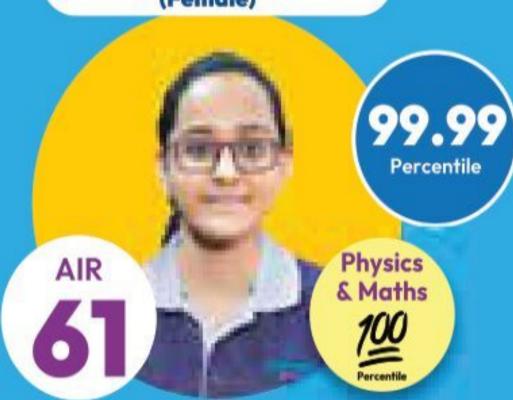




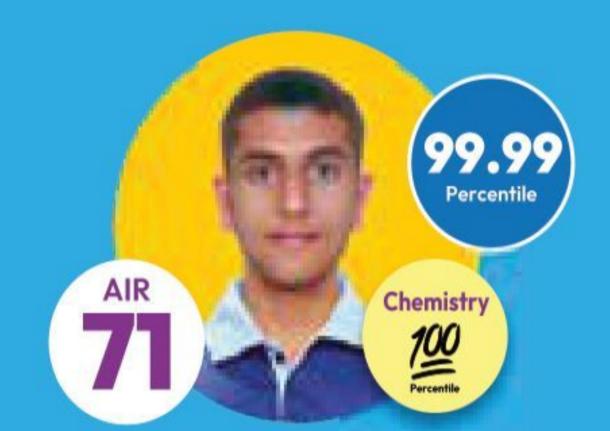


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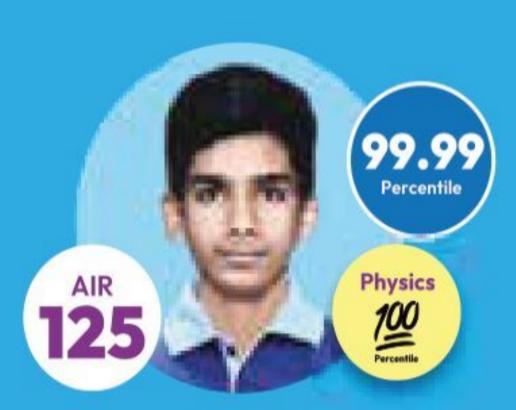
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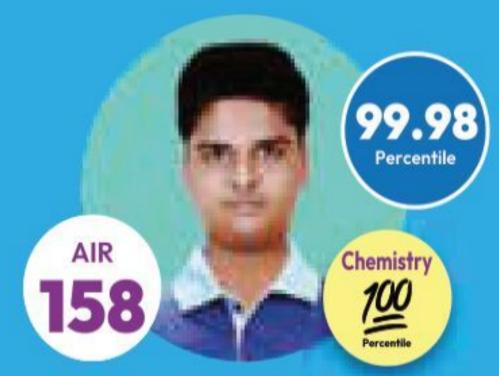
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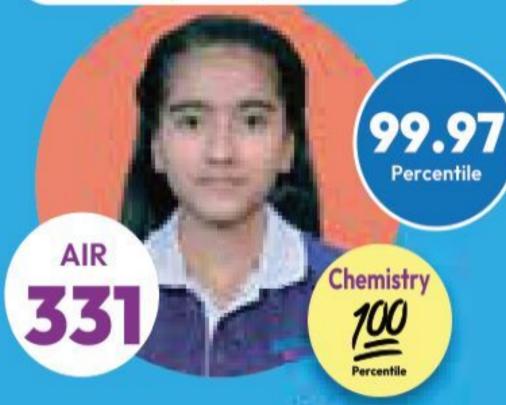


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